# Controlling the Chemoselectivity of Palladium Catalysed Cyclizations of (2-haloanilino)-carbonylic Compounds

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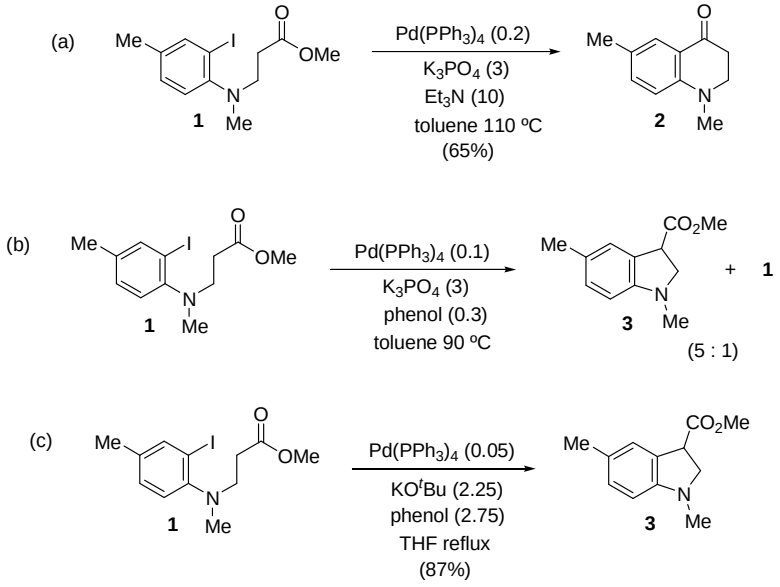
**ABSTRACT.** The factors which control the chemoselectivity of palladium catalyzed cyclizations of (2-haloanilino) carbonylic compounds have been explored by an extensive experimental-computational (DFT) study. It was found that the selectivity of the process, i.e. the formation of fused six versus five-membered rings, can be controlled by the proper selection of the initial reactant, reaction conditions and the additives. Thus, esters or amides produce ketones by a nucleophilic addition process, whereas the addition of $PhO^-$ leads to the formation of indolines by an α-arylation reaction. In contrast, the corresponding ketone reactants yield mixture of both reaction products in the presence of phenol whose ratio depends on the base used. The outcome of the processes can be explained by the formation of a common four-membered palladacycle intermediate from which the competitive nucleophilic addition and α-arylation reactions occur. The remarkable effect of phenol in the process, which makes the α-arylation reaction easier, was found to favor the formation of enol-complexes which are stabilized by an intramolecular hydrogen bond between the hydroxyl group of the enol moiety and the oxygen atom of the phenoxy ligand. Moreover, the chemoselectivy of the process can be also controlled by the addition of bidendate ligands leading to the almost exclusive formation of indoles at expenses of the corresponding alcohols.

## Introduction

Catalytic effectiviness and versatility make palladium a pivotal element in modern organic synthesis. In fact, no other transition metal acts as the catalyst of so many named-reactions.[1] The outcome of the reaction of a given substrate in the presence of a Pd-catalyst can be finely tuned depending both on the catalyst and on the reaction conditions. For example, although aryl- and vinyl-Pd complexes are commonly used as electrophiles in C-C bond forming reactions, their use as nucleophiles in reactions with polar electrophilic multiple bonds has been receiving growing attention during the last years.[2-8]

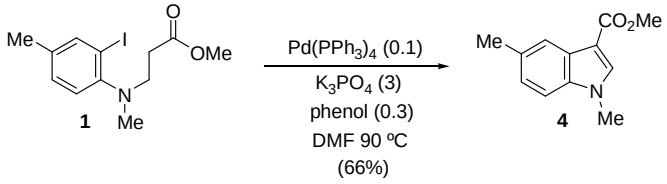
Nevertheless, efforts to exploit the dual character of aryl- and vinyl-Pd intermediates to selectively

unmask their electrophilic or nucleophilic reactivity from the same starting materials have been scarce.[9] Solé and co-workers demonstrated that starting from β-(2-iodoanilino) esters, either the enolate arylation or the nucleophilic substitution at the alkoxycarbonyl group catalyzed by Pd(0) can be selectively promoted by slight modifications of the reaction conditions. Thus, treatment of β-(2-iodoanilino) ester **1** with $Pd(PPh_3)_4$ and $K_3PO_4$ as the base in boiling toluene afforded ketone **2** as a consequence of the formal nucleophilic substitution at the ester group (Scheme 1a).[4a] The addition of a catalytic amount of phenol to the reacting mixture favored the arylation of the enolate to give indoline **3** at the expense of the nucleophilic attack (Scheme 1b).[10] The use of PhOK as the base, generated *in situ* by reaction of PhOH and KO$^t$-Bu, afforded indoline **3** in 87% yield (Scheme 1c).



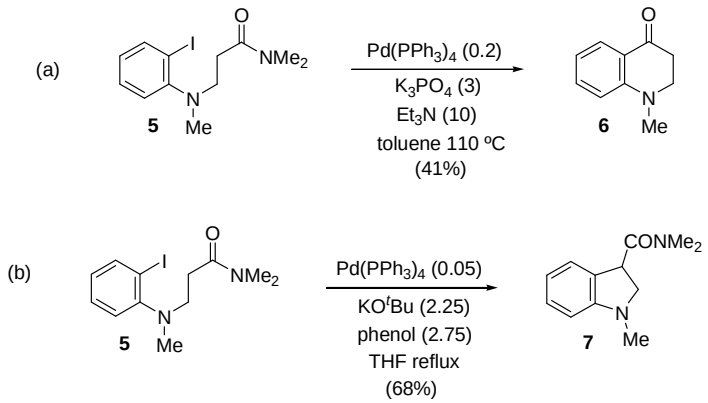

**Scheme 1**

On the other hand, the Pd-catalyzed reaction of **1** using $K_3PO_4$ as the base in the presence of phenol in the more polar solvent DMF directly afforded indole **4**, resulting from the palladium catalyzed dehydrogenation of the initially formed indoline (Scheme 2).



**Scheme 2**

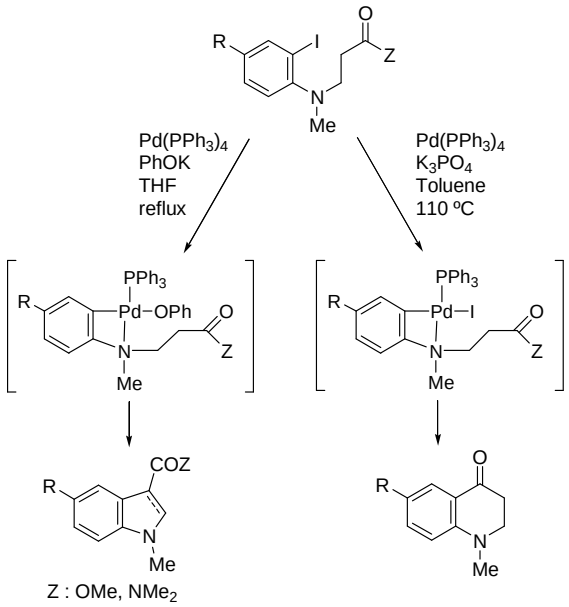
A similar behavior was observed in the reactions of β-(2-iodoanilino) carboxamide **5**, which afforded dihydroquinolone **6** on treatment with $Pd(PPh_3)_4$ and $K_3PO_4$ in toluene, or underwent α-arylation to give indoline **7** when treated with $Pd(PPh_3)_4$ and PhOK as the base in THF (Scheme 3).[5]




**Scheme 3**

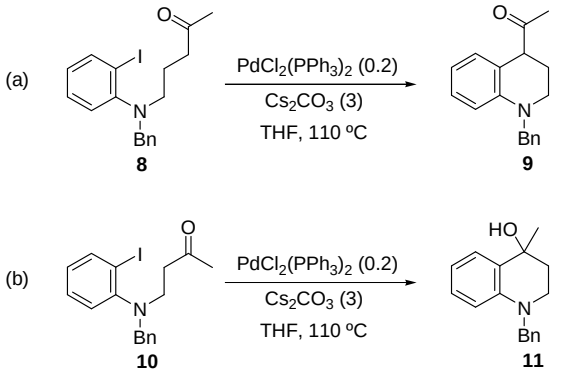
Two major factors seem to be involved in the control of the ambiphilic character of the σ-arylpalladium(II) intermediates in the above transformations. Firstly, the intermediacy of a four-membered azapalladacycle,[11] which strongly modifies the interaction of the metal center with the carbonyl group, might explain the otherwise unexpected attack of the σ-arylpalladium species at the slightly electrophilic carbonyl of esters[4a] and amides[5] (Scheme 4). It should be noted that the above acylation reactions (Schemes 1a and 3a) constitute the first examples of nucleophilic substitution at either the ester or the carboxamido group by a σ-arylpalladium species.

Secondly, the additive phenol would have a beneficial effect on the arylation reaction[12] by exchanging the iodide ligand to give an arylpalladium(II) phenoxide complex. The formation of this transient intermediate would not only stabilize the arylpalladium moiety, preventing the nucleophilic attack at the carbonyl, but also assist the enolization reaction, which would take place in an intramolecular way.




**Scheme 4**

In sharp contrast to that observed with esters and amides, (2-haloanilino)-ketones show a remarkable structure-dependent reactivity in palladium catalyzed cyclizations, since they undergo α-arylation or nucleophilic addition to the carbonyl depending on the length of the tether between the amino and the ketone carbonyl group (Scheme 5).[3d] We have recently carried out computational-DFT studies on these compounds,[13] concluding that the formation of transient four-membered azapalladacyclic intermediates is essential to explain the experimentally observed reaction products.




**Scheme 5**

The above-mentioned examples cleary show the strong effect of phenol or its salts in determining the sense of the cyclization of β-(2-iodoanilino) carboxy-derivatives. Reported herein is the effect of phenol

in the reactivity of β-(2-iodoanilino) ketone **10**, a substrate for which the only previously observed pathway was the nucleophilic addition to the carbonyl. This effect allows to understand the behavior of phenol in the α-arylation reactions and, by extension, the factors controlling the balance between the electrophilic and nucleophilic character of σ-arylpalladium intermediates derived from β-(2-haloanilino) carbonyl compounds. Finally, these results allowed us to elucidate the mechanisms of the intramolecular palladium-catalyzed acylations of aryl halides by esters and amides.

**Results and Discussion**

First, we have computationally studied the effect of phenol in the α-arylation vs. nucleophilic addition reaction pathways of ketone **10M**, a model compound of ketone **10** (Figure 1). This compound was also used by us to unravel the remarkable structure-dependent reactivity observed in the palladium catalyzed cyclizations of (2-iodoanilino) ketones (Scheme 5).[13] Thus, for comparison reasons, Figure 1 gathers the corresponding computed reaction profiles (PCM-B3LYP/def2-SVP level, using THF as solvent) starting from the key four-membered azapalladacyclic intermediate **12** (initially formed from **10M** after the consecutive oxidative addition and cyclization processes)[13] in the presence and absence of $PhO^-$.

Our calculations show that the replacement of the iodide ligand by PhO- leading to complex **13** is clearly exergonic ($\Delta G_{298}$ = -12.3 kcal/mol). This intermediate evolves to complex **14** by coordination of the carbonyl moiety, which forms the palladium alkoxide **15** (which would produce the observed alcohol) through a nucleophilic addition process via transition state **TS1**. As readily seen in Figure 1, the process involving $PhO^-$ as ligand is slightly more difficult than the analogous reaction involving iodide in view of the higher activation barrier of the former transformation ($\Delta\Delta G^{\neq}_{298}$ = 1.6 kcal/mol). This is mainly due to the reduction of the nucleophilicity of the carbon atom directly attached to palladium in complex **14** when the transition metal bears a phenoxy ligand instead of a iodide as seen from the computed NBO-charges at this carbon atom (-0.232 *vs* -0.245, respectively).

We have proposed that the enolate α-arylation process which leads to the corresponding bicyclic

ketone **19** starts with the enolate **17** formed by the base-mediated enolization of complexes **12** and **13** via the corresponding **enol-16**.[13] Interestingly, the formation of ketone **19** directly from **17** via **TS2** is clearly much more difficult for the complex bearing the phenoxy ligand ($\Delta\Delta G^{\neq}_{298}$ = 9.4 kcal/mol). In both cases, this transformation exhibits a higher barrier energy than the nucleophilic addition involving **TS1**, which should be translated in the experiment into a preferential formation of the alcohol derived from **15**. The alternative pathway involving **TS3** from complex **18** seems to be not feasible for the species bearing the phenoxy ligand in view of the clearly endergonic dissociation of the ligand. This contrasts with its iodide-complex counterpart whose dissociation is slightly exergonic.

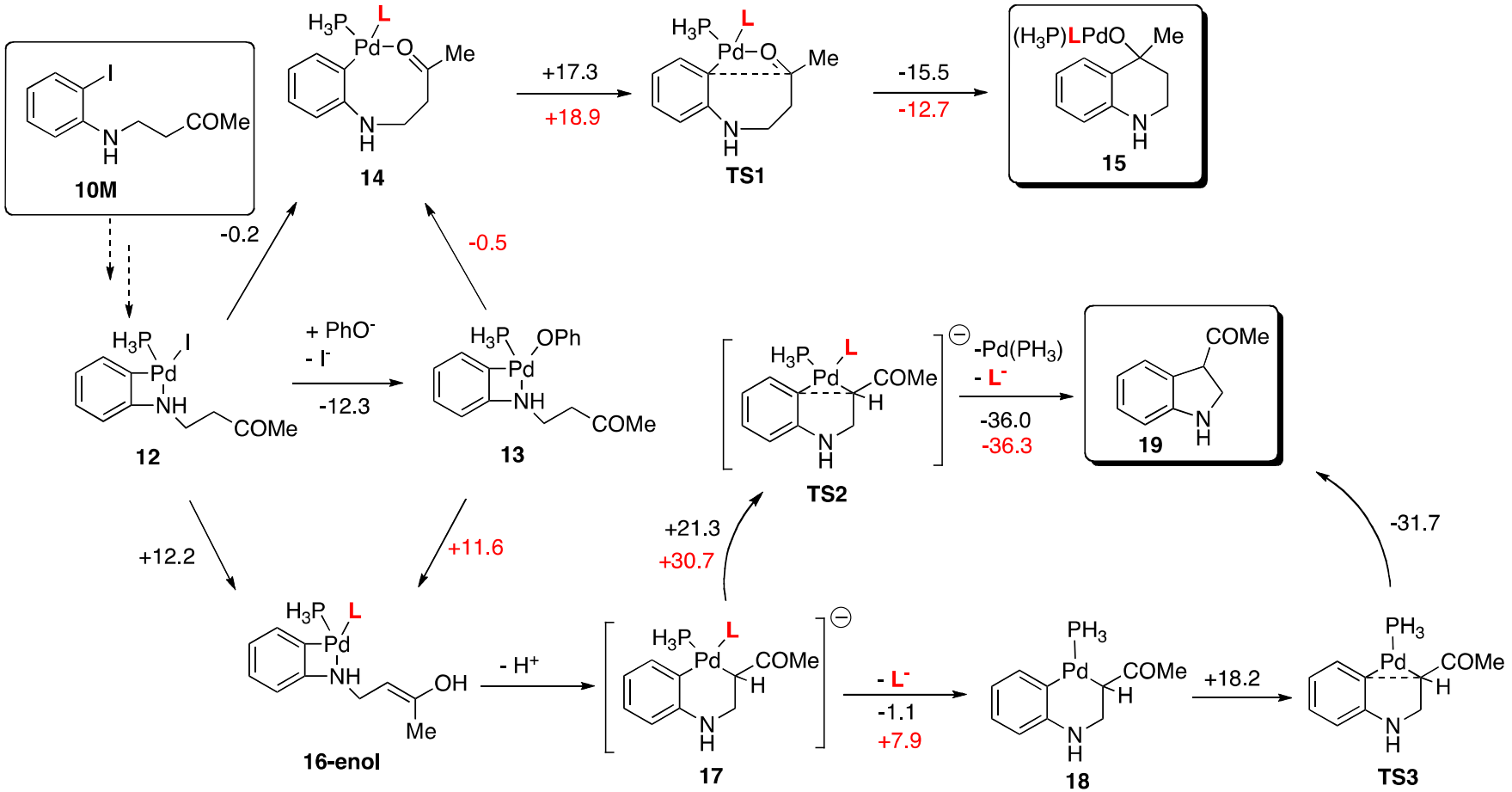
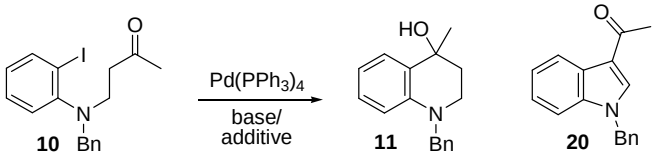



**Figure 1**. Computed reaction profile for the transformation of **12** and **13** into **15** and **19**. Numbers close to arrows indicate the PCM corrected $\Delta G_{298}$ free energies (in kcal/mol) using tetrahydrofuran as solvent. Values in black were computed when L = I whereas values in red indicate the data for L = OPh. All data have been computed at the PCM-B3LYP/def2-SVP level.

It becomes obvious from our computational data that in the presence of the phenoxy ligand the palladium catalyzed reaction of ketone **10** should exclusively produce the corresponding alcohol through the more favourable nucleophilic addition process. To check this prediction, we decided to investigate the reaction of ketone **10** using $Pd(PPh_3)_4$ as the catalyst in the presence of the additive phenol. The most significant results are summarized in Table 1. To our surprise and contrary to what our computational studies had suggested, in no case the exclusive formation of alcohol **11** was observed, as the addition of phenol invariably resulted in the formation of mixtures of ketone **20,** arising from the palladium catalyzed dehydrogenation of the initially formed α-arylation indoline, and alcohol **11**. Moreover, it should be noted that an increase in the amount of phenol resulted in both a high reaction rate and an increase in the formation of the α-arylation product (entries 1 and 3 vs 2 and 4, respectively).

**Table 1.** Pd(0)-Catalyzed Reactions of **10**[a]




| | base/additives (equiv) | solvent/T (ºC) | time | $^1$H NMR ratio | isolated yield (%)[b] |
|---|---|---|---|---|---|
| 1 | $K_3PO_4$ (3)/phenol (0.3) | THF/110 ºC[c] | 24 h | **10** + **11** + **20** (3:5:1) | |
| 2 | $K_3PO_4$ (3)/phenol (3) | THF/110 ºC[c] | 24 h | **11** + **20** (2.5:1)[d] | |
| 3 | $K_3PO_4$ (3)/phenol (0.3) | DMF/90 ºC | 24 h | **11** + **20** (3:1) | |
| 4 | $K_3PO_4$ (3)/phenol (3)[e] | DMF/90 ºC | 24 h | **11** + **20** (1.3:1)[f] | |
| 5 | KO$^t$Bu (2.5)/phenol (2.75) | THF/reflux | 24 h | **11** + **20** (1:1) | **11** + **20** (1:1, 44%)[g] |
| 6 | KO$^t$Bu (1.5)/phenol (3) | THF/70 ºC [h] | 48 h | **11** + **20** (1:2) | **11** + **20** (1:2, 78%) |

[a] The reactions were carried out using $Pd(PPh_3)_4$ (0.1 equiv). [b]Yields refer to products isolated by flash chromatography. [c]The reaction was carried out in a sealed tube. [d]Traces of **10** were also observed in the crude reaction mixture. [e]At 0.05 equiv of $Pd(PPh_3)_4$. [f]The use of *p*-methoxyphenol or *p*-nitrophenol instead of phenol resulted in similar **11**/**20** ratios. [g]*N*-Benzylaniline (42%) was also isolated. [h]At 60 ºC a very low reaction rate was observed whereas the **11**/**20** ratio was not modified.

Although ketone **20** could not be obtained as the single reaction product, we found that the best α-arylation-to-nucleophilic addition ratio was obtained when using KO$^t$Bu as the base in the presence of an excess of phenol in THF (entry 6). Interestingly, the use of a great amount of PhOK did not improve the **20**/**11** ratio but led to an increase in the formation of retro-aza-Michael degradation products (entry 5). These results indicate that a different α-arylation reaction mechanism, which efficiently competes with the nucleophilic addition, must occur in the presence of the phenoxy ligand.

Interestingly, further calculations (Figure 2) show that the double bond of complex **16-enol** can coordinate the transition metal to form the π-complex **21** in an exergonic process ($\Delta G_{298}$ = -3.5 kcal/mol). This compound is stabilized by an intramolecular hydrogen bond between the hydroxyl group of the enol and the oxygen atom of the phenoxy ligand. This interaction was not found in the analogous complex bearing the iodide ligand and for this reason the formation of the respective π-complex is endergonic ($\Delta G_{298}$ = 3.7 kcal/mol). Complex **21** easily evolves to complex **22** where the hydrogen atom of the enol group is transferred to the phenoxy ligand thus resulting in a complex which bears phenol as a ligand. The lower donor ability of the phenol group compared to phenoxy group is nicely reflected in the computed longer Pd–O bond length in **22** compared to **21** (2.318 Å *vs* 2.153 Å, respectively; corresponding Wiberg-bond orders of 0.157 for **22** and 0.273 for **21**). The weakly bonded PhOH in **22** permits its easy dissociation ($\Delta G_{298}$ = -5.9 kcal/mol) leading to complex **18** which produces ketone **19** via **TS3**. If we compare now the corresponding activation barriers of the nucleophilic addition (via **TS1**) and α-arylation (via **TS3** from complex **21**) processes, we can safely conclude that a mixture of products should be produced (as experimentally observed, see above) in view of the practically negligible barrier energy difference ($\Delta\Delta G^{\neq}_{298}$ = 0.7 kcal/mol).

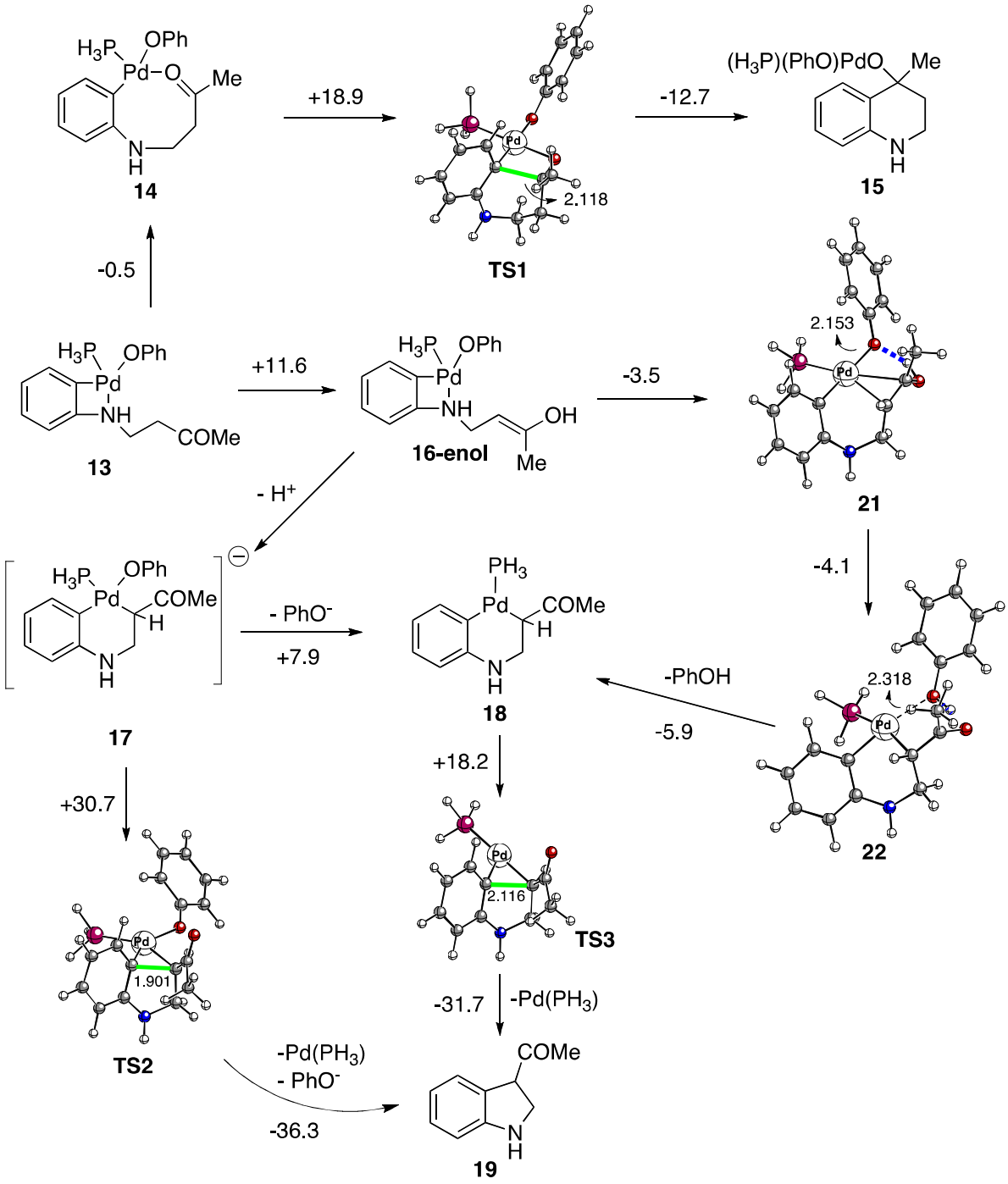
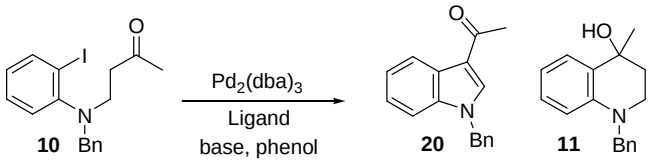


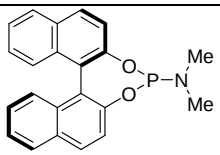
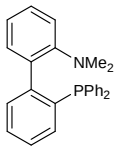
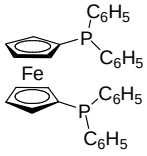
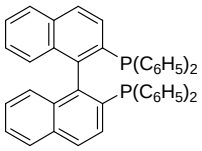
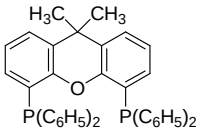

**Figure 2**. Computed reaction profile for the transformation of **13** into **15** and **19**. Numbers close to arrows indicate the PCM corrected $\Delta G_{298}$ free energies (in kcal/mol) using tetrahydrofuran as solvent. Bond lengths are given in Å. All data have been computed at the PCM-B3LYP/def2-SVP level.

Once established the role of the phenoxy additive, different ligands in the palladium catalyzed reaction of ketone **10** were tested to improve the α-arylation-to-nucleophilic addition ratio (Table 2).

The phosphoramidite ligand MONOPHOS[14] was initially chosen with the aim of reducing the nucleophilicity of the carbon atom directly attached to palladium in complex **14** (see Figures 1 and 2). However, the use of this less electron-donating ligand resulted in low conversion of the starting material and the major formation of alcohol **11** (Table 2, entry 1). On the contrary, the use of the bulky and electron-rich ligand $^{t}Bu_3P$ afforded a **20**/**11** ratio (Table 2, entry 2) similar to $PPh_3$ (Table 1, entry 6). When the reaction was carried out with Buchwald's bulky biaryl phosphine $L_1$, a lower reaction rate and decreased **20**/**11** ratio were observed once again (Table 2, entry 3).

**Table 2.** Effect of the Ligand in the Pd(0)-Catalyzed Reactions of **10**




| | ligand | Method[a] | $^{1}$H NMR ratio | isolated yield (%)[b] |
|---|---|---|---|---|
| 1 |  *R*-MONOPHOS | A | **10** + **11** + **20** (4:3:1) | |
| 2 | $(^{t}Bu)_3PH\cdot BF_4$ [c,d] | A | **11** + **20** (1:2.2) | |
| 3 |  $L_1$ | A | **10** + **11** + **20** (1:2.9:4.5) | |
| 4 |  DPPF | A | **10** + **11** + **20** (1:3:1) | |
| 5 |  BINAP | A | **11** + **20** (1:3.9) | **11** (8%), **20** (66%) |
| 6 |  XANTPHOS | A | **11** + **20** (1:14.5) | **20** (80%)[e] |
| 7 | XANTPHOS | B | **11** + **20** (1.3:1) | |
| 8 | XANTPHOS | C | **11** + **20** (1:1.1) | |

[a] Method A: $Pd_2(dba)_3$ (0.05 equiv), ligand (0.1 equiv), KO$^t$Bu (1.5 equiv), and phenol (3 equiv) in THF at 70 ºC for 48 h. Method B: $Pd_2(dba)_3$ (0.05 equiv), ligand (0.1 equiv), $K_3PO_4$ (3 equiv), and phenol (3 equiv) in DMF at 90 ºC for 24 h. Method C: $Pd_2(dba)_3$ (0.05 equiv), ligand (0.1 equiv), and $Cs_2CO_3$ (3 equiv) in THF at 110 ºC in a sealed tube for 24 h. [b] Yields refer to pure products isolated by flash chromatography. [c] At 0.11 equiv of ($^t$Bu)$_3$PH·$BF_4$. [d] 29 h. [e] Alcohol **11** was not isolated during the purification process.

Given the unsaturated nature of complex **18** (see Figure 2), we also decided to test some bidentate phosphines.[15] While the use of dppf resulted in the recovery of significant amounts of the starting material and the major formation of alcohol **11** (Table 2, entry 4), both BINAP and XANTPHOS gave complete conversion and the opposite chemoselectivity (Table 2, entries 5 and 6). The highest α-arylation-to-nucleophilic addition ratio was obtained using XANTPHOS as the ligand, which afforded the desired product **20** in 80% yield in a highly chemoselective transformation (1:14.5 ratio).

In view of the high efficiency of XANTPHOS in promoting the α-arylation of ketone **10**, we decided to study this ligand in the presence of bases other than PhOK. When using XANTPHOS and the $K_3PO_4$/phenol couple in DMF a 1.3:1 mixture of alcohol **11** and ketone **20** was obtained (Table 2, entry 7). This is exactly the same as the α-arylation-to-nucleophilic addition ratio obtained in the reaction of **10** with the ligand $PPh_3$ under analogous conditions (see Table 1, entry 4). Interestingly, the use of XANTPHOS and $Cs_2CO_3$ as the base in the absence of phenol in THF afforded a nearly equimolecular mixture of alcohol **11** and ketone **20** (Table 2, entry 8). In contrast, as shown in Scheme 5b, the use of $PPh_3$ as the ligand in these same reaction conditions gives rise exclusively to the nucleophilic addition to the carbonyl to give **11**.[3d] These results not only confirm the required presence of the phenoxy ligand to overcome the nucleophilic addition to the ketone carbonyl and selectively promote the α-arylation reaction, but also show that changing the ligand opens the way to controlling the ambiphilic character of σ-arylpalladium(II) complexes.

To gain more insight into effect of XANTPHOS in the process, we computationally studied the palladium-catalyzed key processes involving ketone **10M** in the presence of a model xantphos where the phenyl groups attached to the phosphorous atoms and the methyl groups were replaced by hydrogen

atoms (see Figure 3). According to the above discussed reaction profiles, we found that the coordination of the bidentate ligand to the transition metal has a negligible effect on the activation barrier of the α-arylation reaction (via **TS3-xant** compared to analogous process involving **TS3**, Figure 2). On the other hand, the presence of the phenoxy ligand avoids the coordination of the second phosphine moiety of xantphos in **14-xant-A**[16] and therefore, a similar barrier energy ($\Delta G^{\neq}_{298}$ = 17.0 kcal/mol) was computed for the nucleophilic addition reaction (compared to the analogous process involving **14** and **TS1**, Figure 2). Thus, the low computed activation barrier difference ($\Delta\Delta G^{\neq}_{298}$ = 1.3 kcal/mol) suggests the formation of a mixture of reaction products **11**:**20** enriched in the corresponding indol **20**.

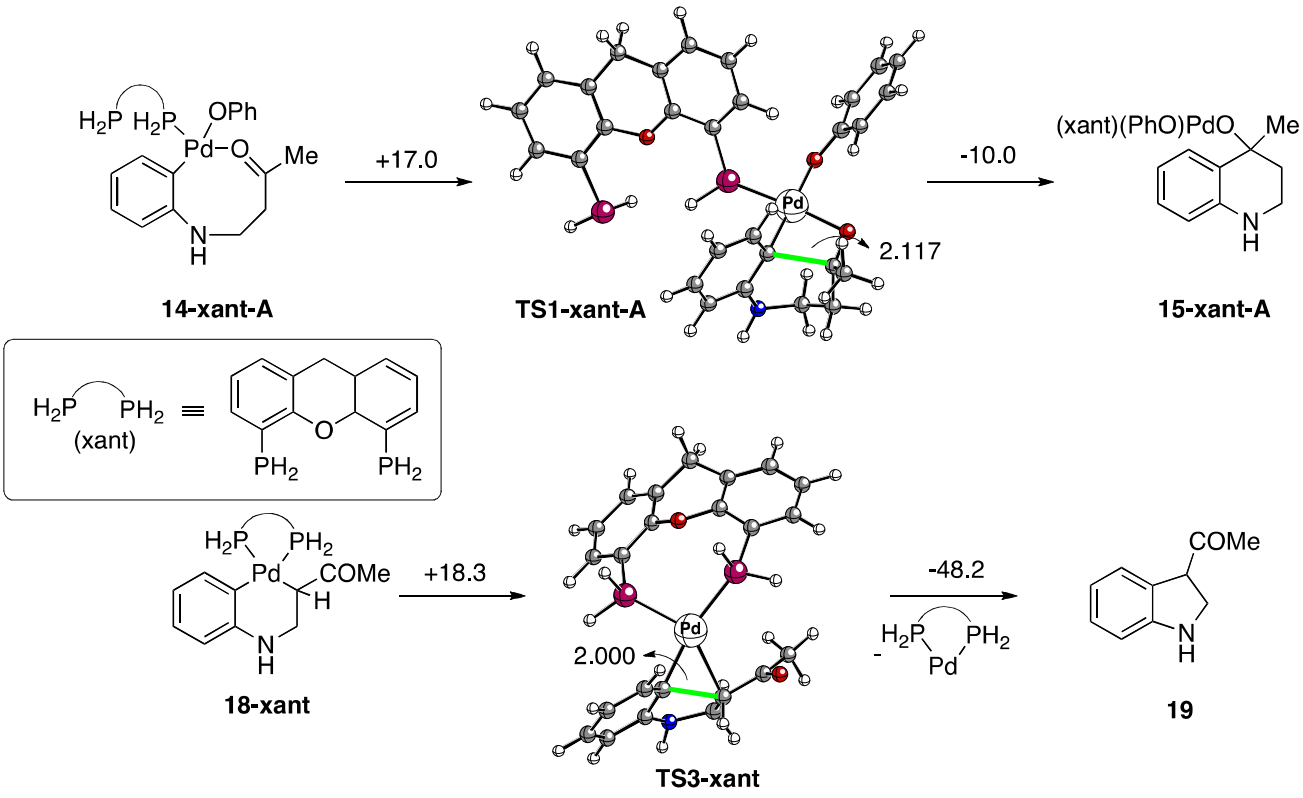



**Figure 3.** Computed reaction profile for the transformations of **14-xant-A** and **18-xant**. Numbers close to arrows indicate the PCM corrected $\Delta G_{298}$ free energies (in kcal/mol) using tetrahydrofuran as solvent. All data have been computed at the PCM-B3LYP/def2-SVP level.

However, a **11:20** ratio of 1:14.5 was experimentally observed which indicates that a different reaction pathway should occur for the nucleophilic addition reaction. Thus, it can be assumed that the

bidentate xantphos ligand coordinates the palladium center to form complex **23-I** after the oxidative addition process (Figure 4). Then, the coordination of the nitrogen atom to the transition metal forms the key four-membered intermediate complex **25** similar to complexes **12** or **13**. This step, which can be viewed as a formal nucleophilic substitution reaction, occurs via **TS-xant** (activation barrier of 6.6 kcal/mol) from complex **24**,[17] which is formed after the loss of the iodide ligand in **23-I** or phenony ligand in **23-OPh**. We were not able to locate a transition state involving the concerted nucleophilic addition and elimination of the nucleophugue either form **23-I** or **23-OPh**. According to the above-described reaction mechanism, cationic complex **25** is transformed into complex **14-xant-B** where the carbonyl group of the ketone is now coordinated to the metal and from which the nucleophilic addition process, through **TS1-xant-B**, occurs. The corresponding computed activation barrier is quite high ($\Delta G^{\neq}_{298}$ = 43.6 kcal/mol, Figure 4) making this process not feasible. Therefore, the α-arylation process is clearly favored in the presence of xantphos as experimentally observed. The small quantity of alcohol **11** produced in these reaction conditions may be derived from the mono-coordination of xantphos through the reaction profile shown in Figure 3.

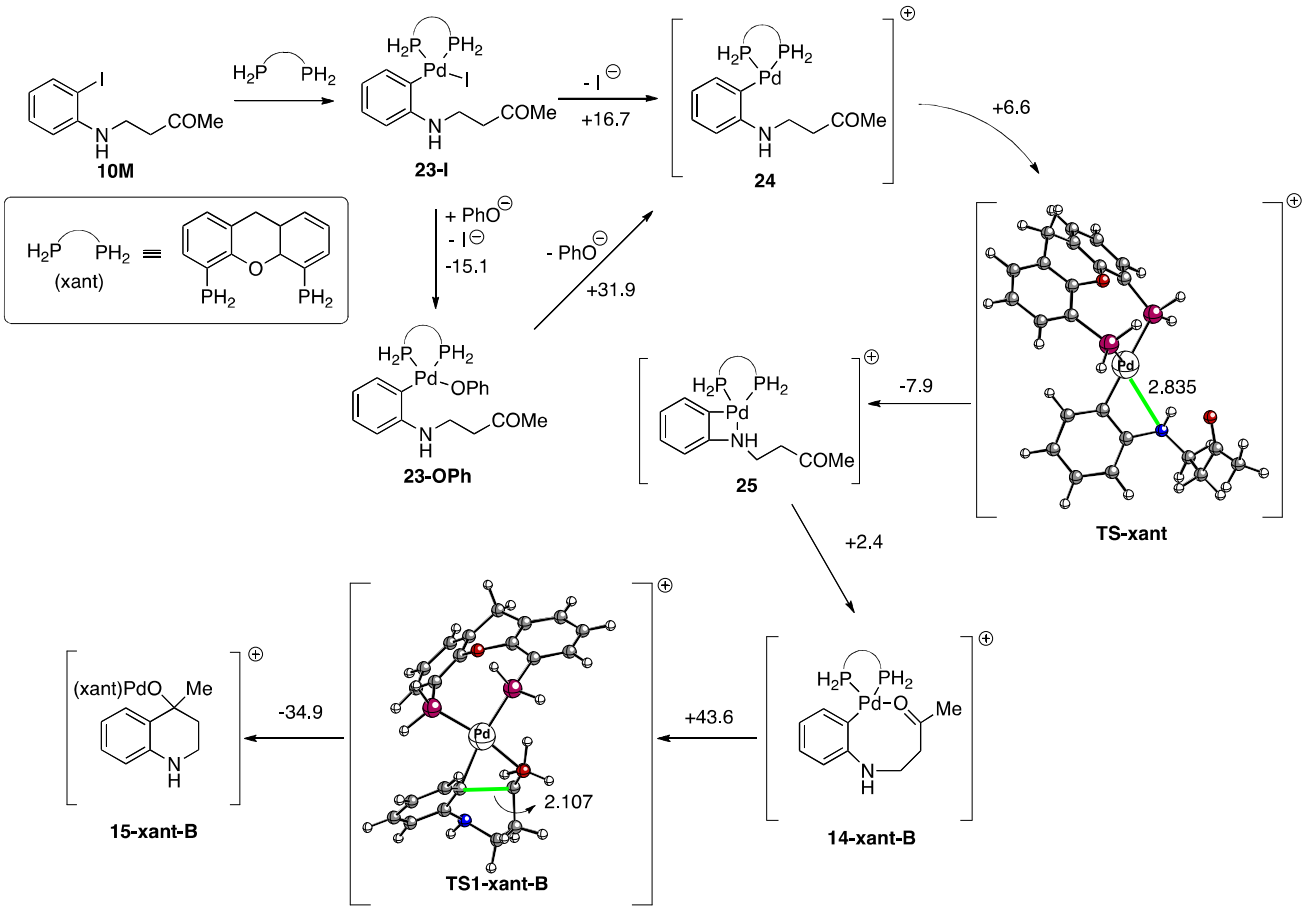



**Figure 4.** Computed reaction profile for the transformation of **10M** to **15-xant-B**. Numbers close to arrows indicate the PCM corrected $\Delta G_{298}$ free energies (in kcal/mol) using tetrahydrofuran as solvent. All data have been computed at the PCM-B3LYP/def2-SVP level.

To complete this study, the Pd-catalyzed cyclization of ester **1M**, a model compound of **1**, was finally considered. The experimental result indicates that cyclization of ester **1** in the presence of $PhO^-$ produces exclusively indoline **3** (see Scheme 1). Our calculations suggest that the corresponding azapalladacycle **13-ester** may evolve to the eight-membered palladacycle **14-ester** (in an endergonic process, $\Delta G_{298}$ = +3.1 kcal/mol) which undergoes the nucleophilic addition via **TS1-ester** yielding complex **15-ester** (Figure 5). Interestingly, the computed higher barrier and reaction energies of this transformation compared to the analogous process involving ketone **14** (($\Delta\Delta G^{\neq}_{298}$ = 5.0 kcal/mol and $\Delta\Delta G_{R,298}$ = 7.9 kcal/mol, see Figures 1 and 5) indicate that the replacement of the ketone group by an

ester makes the nucleophilic addition reaction much more difficult. This is in agreement with our chemical intuition that an ester group is less electrophilic than a ketone.

In contrast, the α-arilation reaction, which proceeds from complex **18-ester** (formed after the corresponding release of phenol in the π-complex **22-ester**) through **TS3-ester**, occurs with an activation barrier which is lower than the analogous process involving the ketone **18** (($\Delta\Delta G^{\neq}_{298}$ = 6.1 kcal/mol) and more importantly, much lower than the corresponding nucleophilic addition involving **TS1-ester** (($\Delta\Delta G^{\neq}_{298}$ = 11.8 kcal/mol). Therefore, the α-arilation process is clearly kinetically favored respect to the nucleophilic addition reaction and as a consequence, the Pd-catalyzed cyclization of ester **1** should yield exclusively indoline **3**, as experimentally observed (Scheme 1).

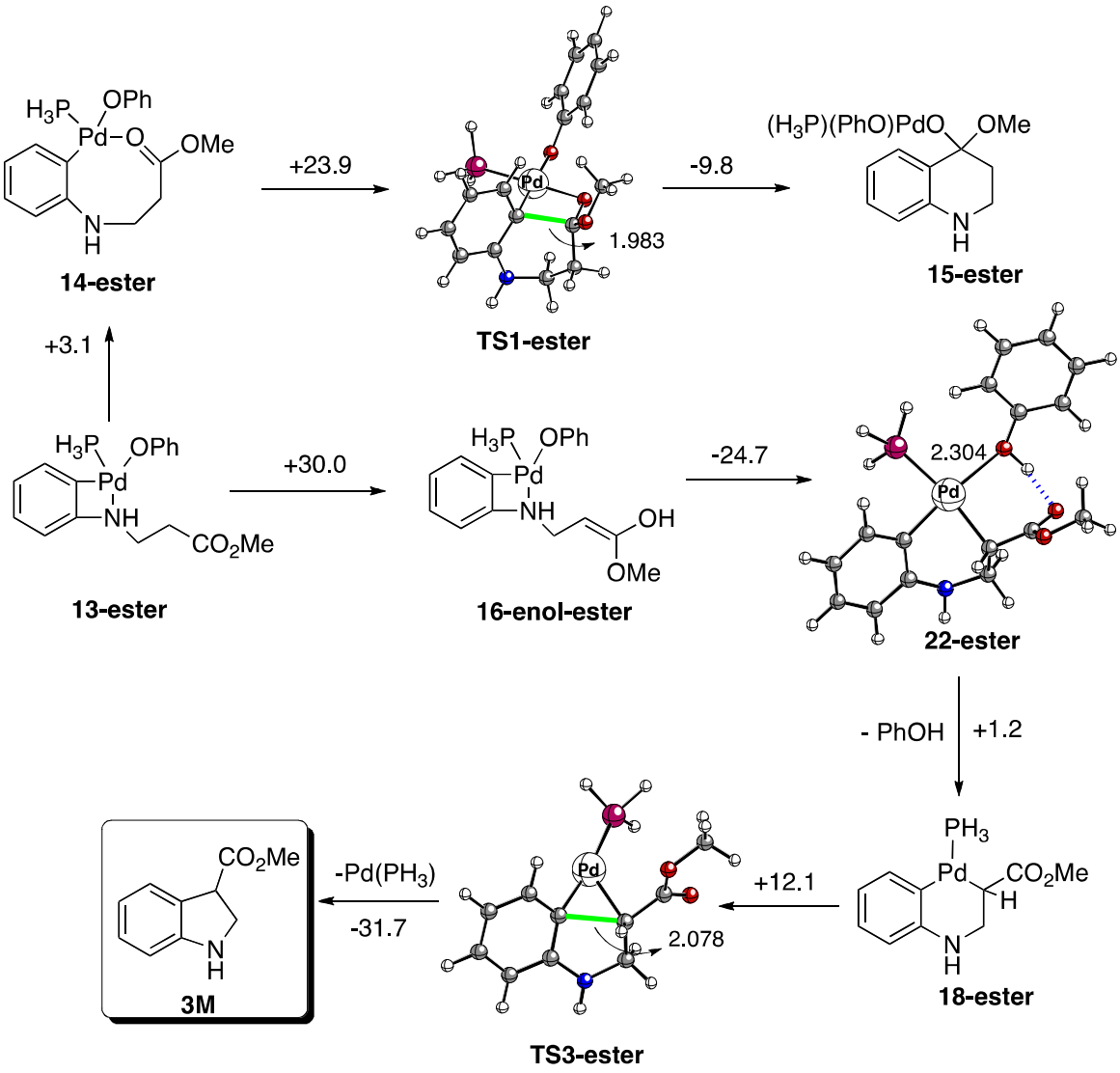



**Figure 5.** Computed reaction profile for the transformation of **13-ester** into **15-ester** and **3M**. Numbers close to arrows indicate the PCM corrected $\Delta G_{298}$ free energies (in kcal/mol) using toluene as solvent. All data have been computed at the PCM-B3LYP/def2-SVP level.

The corresponding reaction profile of the same model ester was computed in absence of $PhO^-$ as well (Figure 6). It was experimentally observed that the treatment of β-(2-iodoanilino) ester **1** with $Pd(PPh_3)_4$ and $K_3PO_4$ as the base in toluene afforded exclusively ketone **2** with no traces of the corresponding α-arylation reaction products (Scheme 1a).[4a] A similar result was obtained (albeit in lower reaction yields) when the reaction was conducted in tetrahydrofuran as solvent. As readily seen in Figure 6, the activation barrier of the nucleophilic addition reaction (via **TS1**) is quite similar to that for the α-

arylation process involving **TS2** and clearly higher than the analogous transformation through **TS3** after iodide dissociation (which seems to be not feasible in toluene but likely in tetrahydrofuran solution). These data are not in agreement with the experimentally observed exclusive formation of ketone **2** (from complex **15**) and therefore, the selectivity must occur in a different reaction step. It can be suggested that the base-mediated ($K_3PO_4$/$Et_3N$, see Scheme 1) formation of anionic complex **17-ester-I** from the four-membered azapalladacyclic intermediate **12-ester** is quite difficult due in view of the computed highly endergonic enolization step ($\Delta G_{298}$= +28.5 and +30.3 kcal/mol, in THF and toluene, respectively). This would switch off the α-arylation pathway making the nucleophilic addition reaction the only possible mechanism. Differently, the enolization is much easier when using ketones as reactants ($Cs_2CO_3$ as base, see Scheme 5a) and as a consequence, α-arylation products can be produced.[3d],[13]

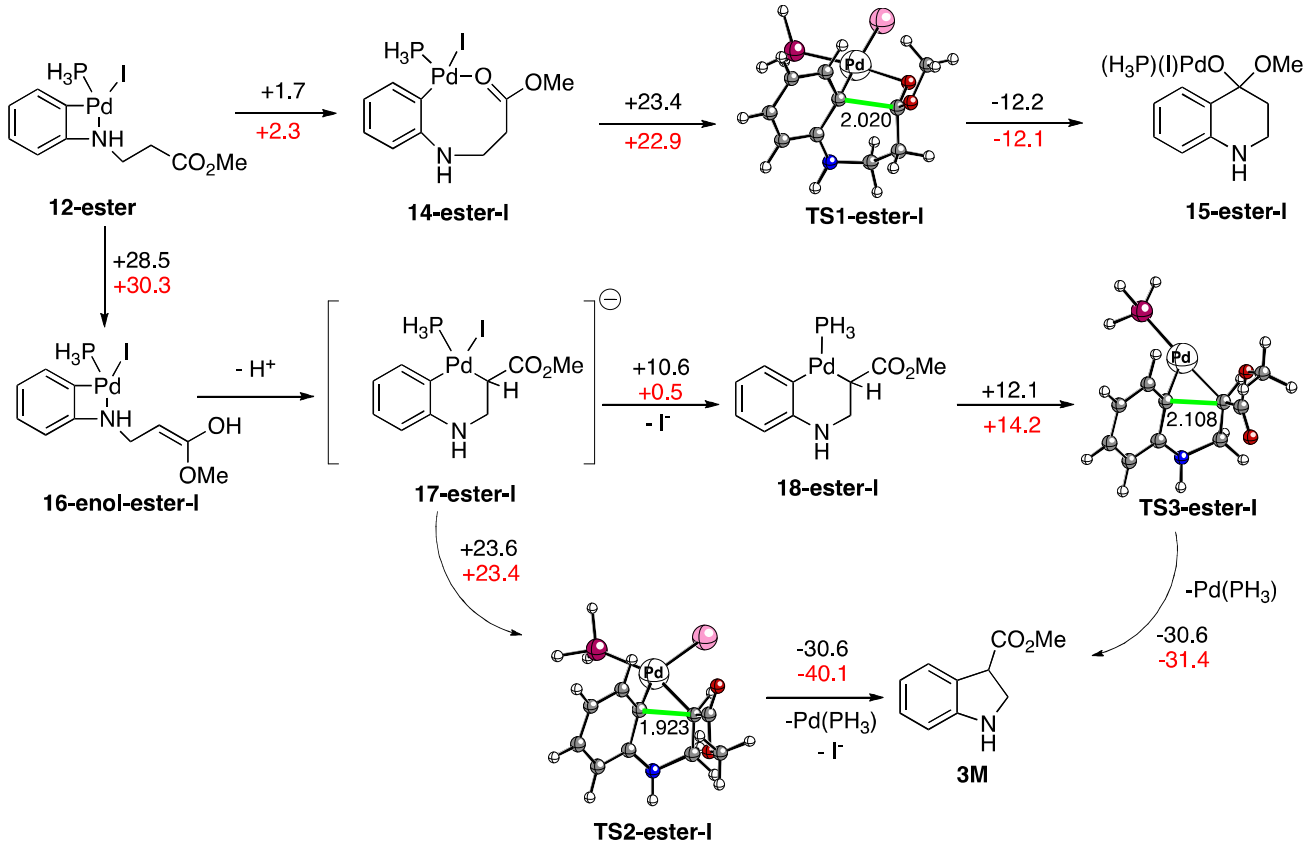



**Figure 6.** Computed reaction profile for the transformation of **12-ester** into **15-ester-I** and **3M**. Numbers close to arrows indicate the PCM corrected $\Delta G_{298}$ free energies (in kcal/mol) using toluene

(black values) or tetrahydrofuran (red values) as solvent. All data have been computed at the PCM-B3LYP/def2-SVP level.

## Conclusions

The joint computational-experimental study reported herein has allowed us to gain a deeper insight into the intimacies of the palladium catalyzed cyclizations of β-(2-haloanilino) carbonylic compounds. The chemoselectivity of the processes, i.e. the nucleophilic attack to the carbonyl *vs.* the α-arylation reaction, can be modified by the proper selection of the reactant, additives and reaction conditions. Thus, esters and amides produce either indolines, by the α-arylation reaction, or dihydroquinolones, through a nucleophilic substitution process, depending on the presence or the absence of phenol in the reaction media. In contrast, the corresponding ketone reactant gives rise to a mixture of the nucleophilic addition alcohol and the α-arylation indole even in the presence of phenol, the product ratio depending on the base used. However, this ratio can be tuned using bidentate phosphines as illustrated by the complete conversion and opposite chemoselectivity provided by both BINAP and XANTPHOS ligands. The outcome of all these processes is nicely explained by the formation of a common four-membered palladacycle intermediate, from which the competitive nucleophilic attack and α-arylation reaction occur. Finally, the effect of phenol in the process was found to favor the formation of enol-complexes which are stabilized by an intramolecular hydrogen bond between the hydroxyl group of the enol moiety and the oxygen atom of the phenoxy ligand thus making the α-arylation process much easier.

## Computational Details

All the calculations reported in this paper were obtained with the GAUSSIAN 09 suite of programs.[18] Electron correlation was partially taken into account using the hybrid functional usually denoted as B3LYP[19] using the double-ζ quality plus polarization def2-SVP basis set[20] for all atoms

(this basis sets include effective core potentials, ECPs, for palladium and iodine atoms). Reactants and products were characterized by frequency calculations,[21] and have positive definite Hessian matrices. Transition structures (TS's) show only one negative eigenvalue in their diagonalized force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration using the Intrinsic Reaction Coordinate (IRC) method.[22] The Wiberg bond indices *Bi* and atomic charges were computed using the natural bond orbital (NBO)[23] method. Solvents effects were taken into account using the Polarizable Continuum Model (PCM).[24] Single point calculations (PCM-B3LYP/def2-SVP) on the gas-phase optimized geometries were performed to estimate the change in the Gibbs energies in the presence of tetrahydrofuran or toluene as solvent.

**Experimental Section**

**General Methods.** All commercially available reagents were used without further purification. β-aminoketone **10** and alcohol **11** are known compounds.[3d] $^{1}$H- and $^{13}$C NMR spectra were recorded in $CDCl_3$ solution, using $Me_4Si$ as the internal standard. Chemical shifts are reported in ppm downfield (δ) from $Me_4Si$. TLC was carried out on $SiO_2$, and the spots were located with UV light.

**Representative Procedure for the Pd(0)-Catalyzed α-Arylation of Ketone 10 Using KO-*t*-Bu as the Base (Table 2, Entry 6).** To a solution of ketone **10** (75 mg, 0.198 mmol) in THF (10 mL) were added under argon phenol (57 mg, 0.60 mmol), KO-*t*-Bu (0.30 mmol, 0.3 mL of 1M solution in *tert*-butyl alcohol), $Pd_2(dba)_3$ (9 mg, 0.01 mmol), and xantphos (11.5 mg, 0.02 mmol). The solution was heated at 75 ºC for 48 h. After being cooled at room temperature, the mixture was diluted with $CH_2Cl_2$ and washed with saturated aqueous $NaHCO_3$ and 1N aqueous NaOH. The organic layer was dried and concentrated. The residue was purified by flash chromatography ($SiO_2$, $CH_2Cl_2$-MeOH 0.5%) to give indole **20** (39.5 mg, 80%). $^{1}$H NMR (300 MHz) δ 2.52 (s, 3H), 5.35 (s, 2H), 7.15 (m, 2H), 7.24-7.38 (m, 6H), 7.75 (s, 1H), 8.40 (dm, *J* = 7.8 Hz, 1H). $^{13}$C NMR (75.4 MHz) δ 27.6 ($CH_3$), 50.7 ($CH_2$), 110.1 (CH), 117.5 (C), 122.6 (2 CH), 123.4 (CH), 126.4 (C), 126.9 (2 CH), 128.2 (CH), 129.0 (2 CH), 134.9

(CH), 135.7 (C), 137.0 (C), 193.0 (C). Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.78; H, 6.33; N, 5.52.

**Acknowledgments**. Support for this work under grants CTQ2010-20714-C02-01/BQU, CSD2007-0006 (Programa Consolider-Ingenio 2010) from the MEC (Spain) and (P2009/PPQ1634-AVANCAT) from the CAM, and CTQ2009-07175 from the MEC (Spain) is gratefully acknowledged. Dr. I. Fernández is a Ramón y Cajal fellow.

**Supporting Information Available.** Cartesian coordinates (in Å) and total energies (in a. u., non corrected zero-point vibrational energies included) of all the stationary points discussed in the text and complete reference [18].

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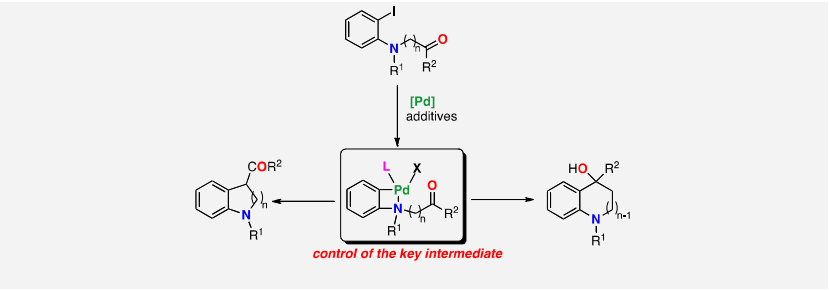
## SYNOPSIS TOC

**Palladium Catalysis**

*Daniel Solé,* Israel Fernández,* and Miguel A. Sierra* Page – Page

**Controlling the Chemoselectivity of Palladium Catalysed Cyclizations of (2-haloanilino)-carbonylic Compounds**




**Pd-controlled!**

The chemoselectivity of the palladium-catalysed cyclizations can be controlled by the proper selection of the reactants, additives, and reaction conditions.

These factors have a great impact on the key palladacycle intermediate (see Figure), from which the competitive reaction pathways (i.e. α-arylation vs nucleophilic addition) occur.

Supporting information belonging to the manuscript:

# Controlling the Chemoselectivity of Palladium Catalysed Cyclizations of (2-haloanilino)-carbonylic Compounds

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Cartesian Coordinates and free energies (ΔG, 298 K) of all stationary points discussed in the text page 3

**Reference [18]:**

[18] Gaussian 09, rev. B.01., M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

Cartesian coordinates (in Å) and Gibbs energies (in a. u., 298 K) of all the stationary points discussed in the text. All calculations have been performed at the B3LYP/def2-SVP level of theory.

**13:** E= -1295.284160

| | | | |
|---|---|---|---|
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| C | -2.424170000 | -0.749265000 | -0.753293000 |
| C | -3.789561000 | -0.833204000 | -1.013061000 |
| C | -4.491852000 | -1.892166000 | -0.418566000 |
| C | -3.826576000 | -2.813734000 | 0.399544000 |
| C | -2.449490000 | -2.699892000 | 0.652478000 |
| Pd | 0.043457000 | -0.737715000 | 0.003655000 |
| N | -1.469493000 | 0.238722000 | -1.271657000 |
| C | -1.776652000 | 1.680373000 | -1.146124000 |
| C | -1.600826000 | 2.194737000 | 0.276308000 |
| C | -1.983894000 | 3.660908000 | 0.418810000 |
| O | -2.497629000 | 4.275426000 | -0.491491000 |
| H | -4.391116000 | -3.635155000 | 0.850112000 |
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| H | -4.301544000 | -0.110914000 | -1.654554000 |
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| H | 0.540220000 | -2.600880000 | 2.538162000 |
| H | 1.708912000 | -3.294515000 | 0.867503000 |
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**14:** E= -1295.282650

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| C | 1.940996000 | 1.614044000 | -1.653348000 |
| C | 1.905049000 | 2.786491000 | -0.654922000 |

| | | | |
|---|---|---|---|
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| H | 3.318471000 | -3.363192000 | 2.091719000 |
| C | 1.679451000 | 3.563616000 | 1.788897000 |
| P | -0.653362000 | -1.983496000 | -1.189654000 |
| H | 3.880002000 | 0.886967000 | -1.730259000 |
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| H | 2.113679000 | 2.045764000 | -2.652430000 |
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| H | 1.029012000 | 3.430830000 | 2.662629000 |
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| H | -4.019221000 | 1.710385000 | -1.462439000 |
| H | -2.413339000 | -1.017946000 | 1.462754000 |
| H | -6.323422000 | 0.948957000 | -0.905975000 |
| H | -4.706688000 | -1.804038000 | 1.994142000 |
| H | -6.688548000 | -0.824672000 | 0.822653000 |

**TS1:** E= -1295.254132

| | | | |
|---|---|---|---|
| C | 1.835184000 | -0.318950000 | 1.864133000 |
| C | 1.845028000 | -0.041675000 | 0.473597000 |
| C | 2.970189000 | -0.483319000 | -0.284138000 |
| C | 3.990888000 | -1.236774000 | 0.349847000 |
| C | 3.917470000 | -1.519413000 | 1.705266000 |
| C | 2.839500000 | -1.051271000 | 2.482673000 |
| Pd | -0.105621000 | -0.129679000 | -0.318347000 |
| N | 3.072882000 | -0.170058000 | -1.616397000 |
| C | 2.321331000 | 0.942374000 | -2.165894000 |
| C | 2.312747000 | 2.148517000 | -1.214124000 |
| C | 1.418350000 | 1.981580000 | 0.016327000 |
| O | 0.146641000 | 1.913417000 | -0.188648000 |
| H | 2.797075000 | -1.262827000 | 3.553470000 |
| C | 1.870415000 | 2.726903000 | 1.258573000 |
| P | -0.405182000 | -2.371157000 | -0.448559000 |
| H | 3.964144000 | -0.373953000 | -2.051958000 |
| H | 4.846321000 | -1.582355000 | -0.239156000 |
| H | 4.718030000 | -2.096963000 | 2.175716000 |
| H | 0.995664000 | 0.047481000 | 2.463201000 |
| H | 2.769343000 | 1.213540000 | -3.132678000 |
| H | 1.274316000 | 0.646442000 | -2.366286000 |
| H | 3.345079000 | 2.385873000 | -0.912246000 |
| H | 1.907426000 | 3.021504000 | -1.753364000 |
| H | 1.211547000 | 2.497000000 | 2.105283000 |
| H | 2.914573000 | 2.510936000 | 1.523020000 |
| H | 1.778856000 | 3.807713000 | 1.046916000 |
| H | -0.653359000 | -2.881055000 | -1.744936000 |
| H | 0.557784000 | -3.317413000 | -0.004448000 |

| | | | |
|---|---|---|---|
| H | -1.548087000 | -2.855736000 | 0.231283000 |
| O | -2.008087000 | -0.271530000 | -1.110690000 |
| C | -3.095825000 | -0.032268000 | -0.387308000 |
| C | -4.318868000 | -0.643428000 | -0.764349000 |
| C | -3.114152000 | 0.827831000 | 0.738968000 |
| C | -5.492803000 | -0.403447000 | -0.050702000 |
| C | -4.294953000 | 1.051544000 | 1.449341000 |
| C | -5.495125000 | 0.442316000 | 1.065276000 |
| H | -4.315663000 | -1.301236000 | -1.637547000 |
| H | -2.186768000 | 1.327357000 | 1.031261000 |
| H | -6.421317000 | -0.887231000 | -0.369796000 |
| H | -4.277332000 | 1.721437000 | 2.314741000 |
| H | -6.416196000 | 0.624270000 | 1.624411000 |

**15:** E= -1295.276275

| | | | |
|---|---|---|---|
| C | 1.770035000 | -0.332774000 | 1.790277000 |
| C | 1.994301000 | 0.375961000 | 0.574535000 |
| C | 2.910716000 | -0.205213000 | -0.379769000 |
| C | 3.514626000 | -1.453838000 | -0.081337000 |
| C | 3.270928000 | -2.094531000 | 1.125825000 |
| C | 2.393615000 | -1.546049000 | 2.074406000 |
| Pd | -0.014290000 | -0.287730000 | -0.199288000 |
| N | 3.222272000 | 0.454185000 | -1.524603000 |
| C | 2.585220000 | 1.706351000 | -1.900567000 |
| C | 2.375052000 | 2.558519000 | -0.657785000 |
| C | 1.465546000 | 1.840845000 | 0.364639000 |
| O | 0.179163000 | 1.707006000 | -0.162670000 |
| H | 2.204627000 | -2.055291000 | 3.021099000 |
| C | 1.425043000 | 2.644992000 | 1.671898000 |
| P | -0.353806000 | -2.560258000 | -0.314471000 |
| H | 3.766841000 | -0.042130000 | -2.218583000 |
| H | 4.211878000 | -1.887555000 | -0.803665000 |
| H | 3.774898000 | -3.042372000 | 1.334801000 |
| H | 1.118029000 | 0.120598000 | 2.538482000 |
| H | 3.231411000 | 2.217528000 | -2.630193000 |
| H | 1.605485000 | 1.521969000 | -2.380519000 |
| H | 3.352056000 | 2.798051000 | -0.202653000 |
| H | 1.883019000 | 3.502999000 | -0.934327000 |
| H | 0.699906000 | 2.210838000 | 2.374640000 |
| H | 2.411809000 | 2.703042000 | 2.159897000 |
| H | 1.082482000 | 3.666602000 | 1.446263000 |
| H | -0.552651000 | -3.092466000 | -1.611530000 |
| H | 0.557769000 | -3.525794000 | 0.195331000 |
| H | -1.542008000 | -3.014705000 | 0.308077000 |
| O | -1.829668000 | -0.410553000 | -1.135204000 |
| C | -2.945463000 | -0.033674000 | -0.506103000 |
| C | -3.038337000 | 1.148639000 | 0.267183000 |
| C | -4.110538000 | -0.823020000 | -0.660965000 |
| C | -4.249653000 | 1.513206000 | 0.854562000 |
| C | -5.319613000 | -0.435586000 | -0.080613000 |
| C | -5.400692000 | 0.732119000 | 0.685436000 |
| H | -2.141308000 | 1.759721000 | 0.389500000 |
| H | -4.042501000 | -1.731387000 | -1.265574000 |
| H | -4.298799000 | 2.430211000 | 1.449831000 |
| H | -6.208523000 | -1.057110000 | -0.225751000 |
| H | -6.346569000 | 1.030082000 | 1.144641000 |

**16-enol:** E= -1295.262506

| | | | |
|---|---|---|---|
| C | -1.451500000 | -1.546986000 | -0.023186000 |

| | | | |
|---|---|---|---|
| C | -2.110820000 | -0.705683000 | -0.924877000 |
| C | -3.437503000 | -0.877588000 | -1.308298000 |
| C | -4.124231000 | -1.973511000 | -0.764295000 |
| C | -3.484155000 | -2.840702000 | 0.129910000 |
| C | -2.148822000 | -2.632576000 | 0.513486000 |
| Pd | 0.270941000 | -0.529216000 | 0.050797000 |
| N | -1.168848000 | 0.331364000 | -1.362347000 |
| C | -1.566642000 | 1.763901000 | -1.276014000 |
| C | -1.872776000 | 2.199646000 | 0.122087000 |
| C | -3.102898000 | 2.524712000 | 0.556664000 |
| O | -4.165637000 | 2.477275000 | -0.304574000 |
| H | -4.036277000 | -3.691930000 | 0.539117000 |
| P | 1.391925000 | -1.773860000 | 1.555182000 |
| C | -3.418704000 | 2.965108000 | 1.955528000 |
| H | -3.934567000 | -0.186536000 | -1.993338000 |
| H | -5.166547000 | -2.151686000 | -1.041129000 |
| H | -1.682655000 | -3.321091000 | 1.225129000 |
| H | -0.833361000 | 0.135924000 | -2.307536000 |
| H | -0.706885000 | 2.330280000 | -1.668090000 |
| H | -2.430877000 | 1.953107000 | -1.933456000 |
| H | -1.037497000 | 2.256609000 | 0.823353000 |
| H | -3.860210000 | 3.977957000 | 1.959550000 |
| H | -4.151848000 | 2.282283000 | 2.421893000 |
| H | -2.518351000 | 2.979536000 | 2.583345000 |
| H | 2.531583000 | -1.197214000 | 2.165540000 |
| H | 0.703200000 | -2.241757000 | 2.704506000 |
| H | 1.949596000 | -3.004456000 | 1.126707000 |
| O | 1.720866000 | 0.930065000 | -0.097559000 |
| C | 3.021707000 | 0.761674000 | -0.214073000 |
| C | 3.905556000 | 1.790020000 | 0.213732000 |
| C | 3.616100000 | -0.406484000 | -0.763219000 |
| C | 5.286867000 | 1.648879000 | 0.103291000 |
| C | 5.003952000 | -0.538563000 | -0.861257000 |
| C | 5.855478000 | 0.482778000 | -0.429391000 |
| H | 3.463538000 | 2.697719000 | 0.632703000 |
| H | 2.960011000 | -1.197538000 | -1.141114000 |
| H | 5.935677000 | 2.462113000 | 0.443895000 |
| H | 5.424317000 | -1.452442000 | -1.293339000 |
| H | 6.939977000 | 0.377572000 | -0.510899000 |
| H | -4.980549000 | 2.677372000 | 0.171712000 |

**17:** E= -1294.758124

| | | | |
|---|---|---|---|
| C | 3.105360000 | -0.049945000 | -0.474919000 |
| C | 1.972495000 | -0.698386000 | 0.100023000 |
| C | 2.240407000 | -1.820137000 | 0.907031000 |
| N | 3.012590000 | 1.129067000 | -1.192766000 |
| C | 0.708824000 | 1.858275000 | -0.465033000 |
| Pd | 0.063998000 | -0.135450000 | -0.293630000 |
| P | -0.746532000 | -2.365786000 | -0.452844000 |
| C | 3.526956000 | -2.337603000 | 1.126631000 |
| C | 4.613029000 | -1.720586000 | 0.504371000 |
| C | 4.400905000 | -0.590997000 | -0.284728000 |
| H | 1.403773000 | -2.328239000 | 1.398920000 |
| H | 3.872615000 | 1.450474000 | -1.615318000 |
| H | 0.014994000 | -3.314135000 | -1.194800000 |
| H | -0.993814000 | -3.226364000 | 0.658546000 |
| H | -1.990871000 | -2.575165000 | -1.104997000 |
| H | 3.668697000 | -3.213407000 | 1.767160000 |
| H | 5.628818000 | -2.107662000 | 0.635266000 |
| H | 5.255764000 | -0.092443000 | -0.757981000 |

| | | | |
|---|---|---|---|
| C | 1.826747000 | 1.910926000 | -1.495633000 |
| H | 2.180772000 | 2.955376000 | -1.637012000 |
| H | 1.385242000 | 1.612795000 | -2.469646000 |
| C | 0.900924000 | 2.499889000 | 0.866623000 |
| O | -0.026871000 | 3.032574000 | 1.463910000 |
| C | 2.283453000 | 2.496670000 | 1.518385000 |
| H | 2.570762000 | 1.468258000 | 1.787159000 |
| H | 3.062445000 | 2.870125000 | 0.835162000 |
| H | 2.240365000 | 3.117237000 | 2.424701000 |
| H | -0.219094000 | 2.255428000 | -0.898042000 |
| O | -1.882256000 | 0.500393000 | -0.920492000 |
| C | -3.020781000 | 0.244629000 | -0.352261000 |
| C | -3.153440000 | -0.242484000 | 0.985476000 |
| C | -4.244632000 | 0.431181000 | -1.070869000 |
| C | -4.400967000 | -0.533050000 | 1.538831000 |
| C | -5.481182000 | 0.139152000 | -0.502412000 |
| C | -5.582719000 | -0.353815000 | 0.808166000 |
| H | -2.242901000 | -0.351784000 | 1.582188000 |
| H | -4.171473000 | 0.812518000 | -2.093608000 |
| H | -4.451316000 | -0.899632000 | 2.570687000 |
| H | -6.390822000 | 0.296031000 | -1.094167000 |
| H | -6.557258000 | -0.581453000 | 1.249352000 |

**TS2:** E= -1294.714742

| | | | |
|---|---|---|---|
| C | 2.831839000 | -0.366177000 | -0.916249000 |
| C | 1.905780000 | -0.255513000 | 0.167618000 |
| C | 2.314963000 | -0.793370000 | 1.411381000 |
| N | 2.513743000 | 0.435778000 | -2.013537000 |
| C | 1.299375000 | 1.515427000 | -0.163000000 |
| Pd | -0.155969000 | -0.286576000 | -0.128071000 |
| P | -0.559641000 | -2.539074000 | -0.374436000 |
| C | 3.469310000 | -1.584491000 | 1.514662000 |
| C | 4.287135000 | -1.797705000 | 0.400912000 |
| C | 3.978325000 | -1.157347000 | -0.813197000 |
| H | 1.697022000 | -0.619016000 | 2.296075000 |
| H | 3.284366000 | 0.619811000 | -2.646197000 |
| H | 0.412841000 | -3.390341000 | -0.986735000 |
| H | -0.707860000 | -3.354427000 | 0.790739000 |
| H | -1.679527000 | -3.108863000 | -1.059377000 |
| H | 3.725501000 | -2.035853000 | 2.478436000 |
| H | 5.182467000 | -2.421428000 | 0.476836000 |
| H | 4.652140000 | -1.247078000 | -1.672915000 |
| C | 1.708605000 | 1.616409000 | -1.636652000 |
| H | 2.281797000 | 2.542035000 | -1.835191000 |
| H | 0.795423000 | 1.666367000 | -2.251717000 |
| C | 2.074235000 | 2.229727000 | 0.898005000 |
| O | 1.597616000 | 2.444468000 | 1.999631000 |
| C | 3.505044000 | 2.653441000 | 0.584695000 |
| H | 4.087865000 | 1.802459000 | 0.197279000 |
| H | 3.520415000 | 3.445443000 | -0.183027000 |
| H | 3.967721000 | 3.036672000 | 1.503871000 |
| H | 0.243143000 | 1.816129000 | -0.016447000 |
| O | -2.053339000 | 0.811504000 | -0.458750000 |
| C | -3.280116000 | 0.552320000 | -0.150697000 |
| C | -3.667242000 | -0.435429000 | 0.813154000 |
| C | -4.362867000 | 1.258909000 | -0.772498000 |
| C | -5.004945000 | -0.692737000 | 1.108819000 |
| C | -5.693741000 | 0.991350000 | -0.464099000 |
| C | -6.041605000 | 0.010449000 | 0.478145000 |
| H | -2.869212000 | -0.981246000 | 1.326705000 |
| H | -4.100011000 | 2.023712000 | -1.509866000 |

| | | | |
|---|---|---|---|
| H | -5.247071000 | -1.459109000 | 1.855117000 |
| H | -6.483728000 | 1.559215000 | -0.970782000 |
| H | -7.089095000 | -0.195650000 | 0.716736000 |

**19:** E= -517.133822

| | | | |
|---|---|---|---|
| C | 0.966074000 | 0.901966000 | 0.026459000 |
| C | 0.347557000 | -0.266976000 | -0.458938000 |
| C | 1.027847000 | -1.478692000 | -0.472974000 |
| N | 0.072770000 | 1.971188000 | 0.004782000 |
| C | -1.086705000 | 0.065769000 | -0.854639000 |
| C | 2.357191000 | -1.519866000 | -0.022044000 |
| C | 2.973305000 | -0.353017000 | 0.443571000 |
| C | 2.289673000 | 0.870474000 | 0.477668000 |
| H | 0.532408000 | -2.383457000 | -0.835047000 |
| H | 0.451615000 | 2.908097000 | -0.081441000 |
| H | 2.910068000 | -2.461736000 | -0.037084000 |
| H | 4.010016000 | -0.391416000 | 0.788934000 |
| H | 2.780114000 | 1.774082000 | 0.848352000 |
| C | -1.064595000 | 1.618699000 | -0.853471000 |
| H | -2.000552000 | 2.063288000 | -0.480474000 |
| H | -0.919078000 | 1.978208000 | -1.890688000 |
| C | -2.050171000 | -0.612719000 | 0.135657000 |
| O | -2.550779000 | -1.677379000 | -0.150628000 |
| C | -2.312738000 | 0.065082000 | 1.467077000 |
| H | -1.431243000 | 0.607000000 | 1.838736000 |
| H | -3.120291000 | 0.806475000 | 1.337137000 |
| H | -2.653952000 | -0.682779000 | 2.195247000 |
| H | -1.346877000 | -0.341363000 | -1.842322000 |

**18:** E= -988.111847

| | | | |
|---|---|---|---|
| C | -1.600802000 | -1.213175000 | 0.251853000 |
| C | -1.246105000 | 0.093768000 | -0.170134000 |
| C | -2.278534000 | 1.009427000 | -0.422814000 |
| N | -0.626428000 | -2.213283000 | 0.473067000 |
| C | 1.249187000 | -1.336192000 | -0.893819000 |
| Pd | 0.708742000 | 0.597888000 | -0.240192000 |
| P | 0.411301000 | 2.809007000 | 0.511386000 |
| C | -3.627408000 | 0.692304000 | -0.212433000 |
| C | -3.962657000 | -0.576078000 | 0.261713000 |
| C | -2.957689000 | -1.520295000 | 0.476507000 |
| H | -2.038109000 | 2.011919000 | -0.789909000 |
| H | -1.060506000 | -3.074210000 | 0.794487000 |
| H | -0.100316000 | 3.794852000 | -0.375298000 |
| H | -0.473086000 | 3.052081000 | 1.593341000 |
| H | 1.523437000 | 3.552588000 | 0.990946000 |
| H | -4.403172000 | 1.435915000 | -0.413297000 |
| H | -5.006615000 | -0.843183000 | 0.446230000 |
| H | -3.224878000 | -2.526764000 | 0.816043000 |
| C | 0.313458000 | -2.487843000 | -0.622209000 |
| H | 0.876629000 | -3.394770000 | -0.338473000 |
| H | -0.222461000 | -2.728564000 | -1.562179000 |
| C | 2.373880000 | -0.994379000 | -0.040386000 |
| O | 2.951164000 | 0.107307000 | -0.265906000 |
| C | 2.762413000 | -1.839019000 | 1.149351000 |
| H | 1.868526000 | -2.106081000 | 1.733256000 |
| H | 3.227288000 | -2.778959000 | 0.805539000 |
| H | 3.478074000 | -1.291004000 | 1.776414000 |
| H | 1.404779000 | -1.078367000 | -1.949068000 |

**TS3:** E= -1325.235326

| | | | |
|---|---|---|---|
| C | -0.118615000 | 2.852687000 | 0.479872000 |
| C | 0.063912000 | 1.581269000 | -0.083040000 |
| C | 1.331986000 | 1.242860000 | -0.644985000 |
| C | 2.354673000 | 2.223826000 | -0.637380000 |
| C | 2.125686000 | 3.495132000 | -0.115212000 |
| C | 0.885257000 | 3.829003000 | 0.440126000 |
| Pd | -1.523472000 | 0.313384000 | 0.027036000 |
| P | -0.492956000 | -0.867800000 | 1.633278000 |
| N | 1.528832000 | -0.001622000 | -1.216134000 |
| C | 2.804252000 | -0.682626000 | -1.317878000 |
| I | -3.936999000 | -0.867890000 | -0.249627000 |
| H | 0.703824000 | 4.827117000 | 0.848427000 |
| H | 3.338859000 | 1.981342000 | -1.042148000 |
| H | 2.935888000 | 4.230384000 | -0.131390000 |
| H | -1.076259000 | 3.096876000 | 0.953350000 |
| H | 0.717287000 | -0.607065000 | -1.130391000 |
| H | 3.554755000 | -0.009526000 | -1.758795000 |
| H | -1.129696000 | -1.081939000 | 2.889953000 |
| H | -0.194484000 | -2.222804000 | 1.324862000 |
| H | 0.790391000 | -0.478565000 | 2.098847000 |
| C | 3.365680000 | -1.247788000 | 0.030306000 |
| H | 2.569434000 | -1.904097000 | 0.442896000 |
| H | 3.444957000 | -0.392214000 | 0.725202000 |
| C | 4.646860000 | -1.996937000 | -0.085119000 |
| H | 4.592330000 | -3.052347000 | -0.379071000 |
| C | 5.962473000 | -1.512645000 | 0.089262000 |
| O | 6.990633000 | -2.213451000 | -0.053229000 |
| C | 6.192423000 | -0.041284000 | 0.486612000 |
| H | 6.830029000 | 0.431208000 | -0.279901000 |
| H | 5.285496000 | 0.569729000 | 0.612940000 |
| H | 6.769209000 | -0.016062000 | 1.427082000 |
| H | 2.688519000 | -1.514579000 | -2.031021000 |

**21:** E= -1295.273613

| | | | |
|---|---|---|---|
| C | 2.414960000 | -1.759571000 | 0.976869000 |
| C | 2.139037000 | -0.616737000 | 0.212510000 |
| C | 3.217445000 | 0.067939000 | -0.405725000 |
| C | 4.519124000 | -0.467747000 | -0.286022000 |
| C | 4.763340000 | -1.626685000 | 0.449571000 |
| C | 3.713929000 | -2.271269000 | 1.106959000 |
| Pd | 0.236964000 | 0.018145000 | -0.062312000 |
| C | 1.299534000 | 2.012919000 | 0.466683000 |
| C | -0.010091000 | 2.407780000 | 0.683919000 |
| C | -0.641586000 | 2.403057000 | 2.050976000 |
| N | 3.029436000 | 1.235960000 | -1.141051000 |
| C | 2.047357000 | 2.274385000 | -0.813558000 |
| O | -1.771489000 | 0.681727000 | -0.465778000 |
| C | -2.911412000 | 0.048310000 | -0.187703000 |
| C | -3.002833000 | -0.939431000 | 0.821069000 |
| C | -4.211695000 | -1.591994000 | 1.080135000 |
| C | -5.364089000 | -1.278235000 | 0.353864000 |
| C | -5.288050000 | -0.295107000 | -0.641371000 |
| C | -4.085908000 | 0.356231000 | -0.914968000 |
| P | -0.151652000 | -1.986008000 | -1.101345000 |
| O | -0.752574000 | 2.909795000 | -0.303398000 |
| H | 1.902736000 | 1.806208000 | 1.353982000 |
| H | 1.597451000 | -2.279000000 | 1.486305000 |
| H | 3.887959000 | 1.607516000 | -1.528313000 |

| | | | |
|---|---|---|---|
| H | -0.024105000 | -3.193756000 | -0.371621000 |
| H | -1.424409000 | -2.183835000 | -1.691213000 |
| H | 0.688818000 | -2.300241000 | -2.196762000 |
| H | 3.894704000 | -3.164580000 | 1.709832000 |
| H | 5.783416000 | -2.013422000 | 0.522125000 |
| H | 5.351284000 | 0.051815000 | -0.772962000 |
| H | 2.592332000 | 3.232916000 | -0.701382000 |
| H | 1.323433000 | 2.424992000 | -1.630982000 |
| H | -2.111320000 | -1.170601000 | 1.412316000 |
| H | -4.025628000 | 1.116024000 | -1.698394000 |
| H | -4.252093000 | -2.349852000 | 1.868278000 |
| H | -6.180084000 | -0.035412000 | -1.219128000 |
| H | -6.308169000 | -1.787252000 | 0.561457000 |
| H | -0.801652000 | 3.449280000 | 2.363276000 |
| H | -1.630969000 | 1.923498000 | 2.004737000 |
| H | -0.022070000 | 1.893764000 | 2.801740000 |
| H | -1.475123000 | 2.200405000 | -0.465272000 |

**22:** E= -1295.282928

| | | | |
|---|---|---|---|
| C | 3.207700000 | 0.453527000 | -0.351617000 |
| C | 2.301174000 | -0.380320000 | 0.352957000 |
| C | 2.796356000 | -1.307866000 | 1.276427000 |
| C | 4.174480000 | -1.474984000 | 1.483009000 |
| C | 5.068644000 | -0.698380000 | 0.744029000 |
| C | 4.592359000 | 0.257491000 | -0.153804000 |
| Pd | 0.358398000 | -0.255708000 | -0.112433000 |
| C | 0.781171000 | 1.850013000 | 0.198013000 |
| C | -0.545007000 | 2.418240000 | 0.378551000 |
| C | -0.993162000 | 2.767669000 | 1.785544000 |
| N | 2.767281000 | 1.423828000 | -1.245179000 |
| C | 1.537872000 | 2.206105000 | -1.071443000 |
| O | -1.792670000 | 0.113118000 | -0.892010000 |
| C | -3.021545000 | -0.219161000 | -0.376424000 |
| C | -3.981432000 | 0.770604000 | -0.115782000 |
| C | -5.231060000 | 0.404418000 | 0.390736000 |
| C | -5.535435000 | -0.936570000 | 0.643190000 |
| C | -4.572893000 | -1.915993000 | 0.379462000 |
| C | -3.320784000 | -1.565098000 | -0.130502000 |
| P | 0.461920000 | -2.515872000 | -0.779217000 |
| O | -1.338472000 | 2.614997000 | -0.566923000 |
| H | 1.398739000 | 1.958333000 | 1.096494000 |
| H | 2.100139000 | -1.924605000 | 1.852626000 |
| H | 3.520031000 | 1.949000000 | -1.673049000 |
| H | 0.701689000 | -3.526303000 | 0.189525000 |
| H | -0.569732000 | -3.178846000 | -1.500835000 |
| H | 1.538354000 | -2.824914000 | -1.647440000 |
| H | 4.536062000 | -2.205412000 | 2.211043000 |
| H | 6.147133000 | -0.820287000 | 0.876800000 |
| H | 5.300044000 | 0.881263000 | -0.710198000 |
| H | 1.823177000 | 3.277964000 | -1.033340000 |
| H | 0.872085000 | 2.103045000 | -1.945635000 |
| H | -2.574579000 | -2.330959000 | -0.344302000 |
| H | -3.730964000 | 1.816212000 | -0.307624000 |
| H | -4.796886000 | -2.969080000 | 0.568993000 |
| H | -5.973170000 | 1.181868000 | 0.590711000 |
| H | -6.513662000 | -1.216445000 | 1.040577000 |
| H | -1.724844000 | 1.107356000 | -1.000617000 |
| H | -2.055614000 | 2.515740000 | 1.916848000 |
| H | -0.388017000 | 2.276617000 | 2.559939000 |
| H | -0.897589000 | 3.860192000 | 1.913291000 |

**13-ester:** E= -1370.455104

| | | | |
|---|---|---|---|
| C | 5.686854000 | 0.972860000 | -0.358532000 |
| C | 4.893060000 | 2.054307000 | 0.048965000 |
| C | 3.502651000 | 1.963350000 | 0.054561000 |
| C | 2.841030000 | 0.775992000 | -0.357828000 |
| C | 3.660674000 | -0.304401000 | -0.778894000 |
| C | 5.054430000 | -0.203517000 | -0.772660000 |
| O | 1.523160000 | 0.722300000 | -0.349528000 |
| Pd | 0.312434000 | -0.904820000 | 0.011174000 |
| P | 1.637216000 | -1.875894000 | 1.549338000 |
| C | -1.270725000 | -2.122452000 | 0.132910000 |
| C | -2.084149000 | -1.447124000 | -0.782725000 |
| C | -3.396037000 | -1.817984000 | -1.066141000 |
| C | -3.906854000 | -2.936751000 | -0.391181000 |
| C | -3.111958000 | -3.635221000 | 0.526106000 |
| C | -1.793798000 | -3.234186000 | 0.799095000 |
| N | -1.316063000 | -0.341340000 | -1.369404000 |
| C | -1.892144000 | 1.020136000 | -1.366913000 |
| C | -1.886512000 | 1.648406000 | 0.020790000 |
| C | -2.533955000 | 3.015464000 | 0.021993000 |
| O | -2.502476000 | 3.566933000 | 1.247259000 |
| O | -3.020447000 | 3.558715000 | -0.941064000 |
| H | -3.526916000 | -4.507490000 | 1.039335000 |
| H | -4.009568000 | -1.269094000 | -1.785740000 |
| H | -4.930523000 | -3.266333000 | -0.585331000 |
| H | -1.203193000 | -3.798294000 | 1.527295000 |
| H | -1.024451000 | -0.578386000 | -2.318391000 |
| H | -1.282893000 | 1.633782000 | -2.045305000 |
| H | -2.916190000 | 1.008581000 | -1.777496000 |
| H | -2.416488000 | 1.017254000 | 0.753824000 |
| H | -0.850168000 | 1.747963000 | 0.385985000 |
| H | 2.654085000 | -1.084515000 | 2.134901000 |
| H | 1.038864000 | -2.424791000 | 2.712775000 |
| H | 2.405808000 | -2.997047000 | 1.149830000 |
| H | 2.884311000 | 2.805352000 | 0.376135000 |
| H | 3.174815000 | -1.215810000 | -1.142422000 |
| H | 5.368931000 | 2.984945000 | 0.373677000 |
| H | 5.654081000 | -1.055564000 | -1.108453000 |
| H | 6.776713000 | 1.049929000 | -0.358335000 |
| C | -3.073776000 | 4.869708000 | 1.371508000 |
| H | -2.952279000 | 5.158062000 | 2.422876000 |
| H | -2.556892000 | 5.587822000 | 0.717006000 |
| H | -4.140440000 | 4.858063000 | 1.099919000 |

**14-ester:** E= -1370.454610

| | | | |
|---|---|---|---|
| C | -5.641901000 | -0.543049000 | 0.688994000 |
| C | -5.453112000 | 0.219295000 | -0.472184000 |
| C | -4.174981000 | 0.568934000 | -0.902737000 |
| C | -3.016914000 | 0.173410000 | -0.178328000 |
| C | -3.229101000 | -0.590570000 | 1.001375000 |
| C | -4.515888000 | -0.940927000 | 1.417250000 |
| O | -1.825242000 | 0.526811000 | -0.612895000 |
| Pd | -0.006893000 | -0.359129000 | -0.147605000 |
| P | -0.615153000 | -2.323735000 | -1.001957000 |
| C | 1.859719000 | -1.074160000 | 0.209498000 |
| C | 2.030865000 | -2.119208000 | 1.132909000 |
| C | 3.288594000 | -2.581265000 | 1.537989000 |
| C | 4.427215000 | -1.987655000 | 0.991141000 |

| | | | |
|---|---|---|---|
| C | 4.293645000 | -0.951376000 | 0.071574000 |
| C | 3.027002000 | -0.466877000 | -0.333421000 |
| N | 3.036519000 | 0.607227000 | -1.227645000 |
| C | 1.941552000 | 1.224970000 | -1.930120000 |
| C | 1.489570000 | 2.577921000 | -1.354361000 |
| C | 1.038679000 | 2.537199000 | 0.084886000 |
| O | 1.154217000 | 3.708582000 | 0.690093000 |
| O | 0.591825000 | 1.561958000 | 0.673902000 |
| H | 3.371288000 | -3.390916000 | 2.267169000 |
| H | 3.960993000 | 0.902975000 | -1.512030000 |
| H | 5.191770000 | -0.486733000 | -0.350474000 |
| H | 5.425970000 | -2.328346000 | 1.277334000 |
| H | 1.146101000 | -2.586139000 | 1.577047000 |
| H | 2.225467000 | 1.396284000 | -2.983361000 |
| H | 1.083305000 | 0.532288000 | -1.962919000 |
| H | 2.287752000 | 3.332239000 | -1.429968000 |
| H | 0.636243000 | 2.965756000 | -1.940773000 |
| H | -0.054573000 | -2.699396000 | -2.248522000 |
| H | -0.352471000 | -3.510777000 | -0.274937000 |
| H | -1.993755000 | -2.483260000 | -1.282075000 |
| H | -4.029867000 | 1.160390000 | -1.810680000 |
| H | -2.358590000 | -0.883863000 | 1.597373000 |
| H | -6.320545000 | 0.543412000 | -1.056090000 |
| H | -4.639076000 | -1.528899000 | 2.332461000 |
| H | -6.646512000 | -0.817096000 | 1.019993000 |
| C | 0.682068000 | 3.804959000 | 2.044057000 |
| H | 0.845720000 | 4.846878000 | 2.342206000 |
| H | -0.385862000 | 3.549195000 | 2.095573000 |
| H | 1.246930000 | 3.122951000 | 2.695421000 |

**TS1-ester:** E= -1370.414548

| | | | |
|---|---|---|---|
| C | 1.462351000 | 1.709119000 | -0.565230000 |
| C | 1.829813000 | 0.017684000 | 0.401544000 |
| C | 2.922473000 | -0.723479000 | -0.154473000 |
| N | 3.082907000 | -0.784348000 | -1.509833000 |
| C | 2.407584000 | 0.166266000 | -2.378109000 |
| C | 2.394017000 | 1.567466000 | -1.771737000 |
| C | 3.838581000 | -1.381268000 | 0.704415000 |
| C | 3.701455000 | -1.287048000 | 2.080712000 |
| C | 2.659240000 | -0.532529000 | 2.655308000 |
| C | 1.754200000 | 0.104502000 | 1.818853000 |
| Pd | -0.136159000 | -0.348006000 | -0.314075000 |
| P | -0.461673000 | -2.537006000 | 0.172616000 |
| O | 0.183046000 | 1.628321000 | -0.765482000 |
| O | 1.912328000 | 2.732436000 | 0.223016000 |
| H | 2.565777000 | -0.455910000 | 3.740746000 |
| H | 3.936036000 | -1.207674000 | -1.852528000 |
| H | 4.664048000 | -1.954086000 | 0.270640000 |
| H | 4.422191000 | -1.797956000 | 2.725314000 |
| H | 0.937932000 | 0.679720000 | 2.263230000 |
| H | 2.927052000 | 0.173176000 | -3.346965000 |
| H | 1.366832000 | -0.155944000 | -2.571382000 |
| H | 3.410170000 | 1.868749000 | -1.477590000 |
| H | 2.022882000 | 2.288857000 | -2.517688000 |
| H | -0.716496000 | -3.380684000 | -0.934707000 |
| H | 0.493152000 | -3.333645000 | 0.860468000 |
| H | -1.607922000 | -2.808309000 | 0.957409000 |
| C | 0.964270000 | 3.418257000 | 1.028649000 |
| H | 1.522192000 | 4.217340000 | 1.534796000 |
| H | 0.156865000 | 3.848883000 | 0.417782000 |

| | | | |
|---|---|---|---|
| H | 0.511295000 | 2.759849000 | 1.786927000 |
| O | -2.042487000 | -0.665702000 | -1.040692000 |
| C | -3.119722000 | -0.212856000 | -0.409590000 |
| C | -4.355123000 | -0.885076000 | -0.591815000 |
| C | -3.115215000 | 0.932579000 | 0.424672000 |
| C | -5.519185000 | -0.430017000 | 0.027038000 |
| C | -4.285955000 | 1.370892000 | 1.045758000 |
| C | -5.498818000 | 0.698824000 | 0.855294000 |
| H | -4.369671000 | -1.764627000 | -1.240846000 |
| H | -2.176570000 | 1.476082000 | 0.559558000 |
| H | -6.457867000 | -0.968223000 | -0.137567000 |
| H | -4.250603000 | 2.258988000 | 1.684551000 |
| H | -6.412162000 | 1.048857000 | 1.342420000 |

**15-ester:** E= -1370.432693

| | | | |
|---|---|---|---|
| C | -5.424918000 | 0.812681000 | 0.583682000 |
| C | -4.212271000 | 1.451596000 | 0.869890000 |
| C | -3.012873000 | 1.000454000 | 0.317576000 |
| C | -2.994276000 | -0.125923000 | -0.538390000 |
| C | -4.224649000 | -0.770666000 | -0.814756000 |
| C | -5.418002000 | -0.298385000 | -0.267086000 |
| O | -1.889903000 | -0.590541000 | -1.125231000 |
| Pd | -0.069534000 | -0.436419000 | -0.210166000 |
| P | -0.541231000 | -2.663765000 | 0.052149000 |
| C | 1.980642000 | 0.204374000 | 0.443993000 |
| C | 1.727805000 | -0.274870000 | 1.759322000 |
| C | 2.277028000 | -1.469000000 | 2.222124000 |
| C | 3.106192000 | -2.210202000 | 1.364916000 |
| C | 3.389849000 | -1.775963000 | 0.075307000 |
| C | 2.871881000 | -0.547061000 | -0.405198000 |
| N | 3.235193000 | -0.057714000 | -1.617328000 |
| C | 2.730185000 | 1.201101000 | -2.149711000 |
| C | 2.523848000 | 2.202513000 | -1.021090000 |
| C | 1.536010000 | 1.639731000 | 0.023119000 |
| O | 0.279284000 | 1.527926000 | -0.511001000 |
| O | 1.566418000 | 2.416903000 | 1.214281000 |
| H | 2.074422000 | -1.814380000 | 3.237513000 |
| H | 3.773284000 | -0.659903000 | -2.227461000 |
| H | 4.060486000 | -2.354894000 | -0.565745000 |
| H | 3.549448000 | -3.146767000 | 1.715216000 |
| H | 1.133269000 | 0.363025000 | 2.414746000 |
| H | 3.459821000 | 1.579750000 | -2.882020000 |
| H | 1.770317000 | 1.045364000 | -2.676259000 |
| H | 3.483214000 | 2.430171000 | -0.527804000 |
| H | 2.108366000 | 3.133171000 | -1.433676000 |
| H | -0.742364000 | -3.402386000 | -1.139028000 |
| H | 0.310815000 | -3.562589000 | 0.749640000 |
| H | -1.765193000 | -2.935289000 | 0.710174000 |
| H | -2.069816000 | 1.510289000 | 0.526751000 |
| H | -4.214851000 | -1.636564000 | -1.481786000 |
| H | -4.199626000 | 2.323495000 | 1.531039000 |
| H | -6.355599000 | -0.810186000 | -0.504726000 |
| H | -6.360164000 | 1.174712000 | 1.017624000 |
| C | 0.929970000 | 3.676613000 | 1.147562000 |
| H | 0.896824000 | 4.070817000 | 2.173798000 |
| H | 1.489637000 | 4.397374000 | 0.520885000 |
| H | -0.096497000 | 3.594269000 | 0.755889000 |

**16-enol-ester:** E= -1370.408450

| | | | |
|---|---|---|---|
| C | 5.982509000 | 0.791456000 | -0.299666000 |
| C | 5.286632000 | 1.977067000 | -0.022958000 |
| C | 3.894115000 | 2.013426000 | -0.036210000 |
| C | 3.128529000 | 0.853564000 | -0.335480000 |
| C | 3.851442000 | -0.334891000 | -0.625283000 |
| C | 5.248463000 | -0.359712000 | -0.601715000 |
| O | 1.813308000 | 0.923037000 | -0.344641000 |
| Pd | 0.472436000 | -0.590646000 | 0.055905000 |
| P | 1.607024000 | -1.437795000 | 1.806124000 |
| C | -1.149705000 | -1.761461000 | 0.112990000 |
| C | -1.826916000 | -1.173860000 | -0.959744000 |
| C | -3.094338000 | -1.568737000 | -1.378942000 |
| C | -3.702376000 | -2.622218000 | -0.679484000 |
| C | -3.043889000 | -3.232855000 | 0.395411000 |
| C | -1.768780000 | -2.807535000 | 0.802830000 |
| N | -0.976135000 | -0.122225000 | -1.528849000 |
| C | -1.533323000 | 1.254039000 | -1.657289000 |
| C | -1.889177000 | 1.857352000 | -0.335957000 |
| C | -3.149033000 | 2.004532000 | 0.100673000 |
| O | -3.433054000 | 2.420732000 | 1.359388000 |
| O | -4.234460000 | 1.742283000 | -0.681065000 |
| H | -3.532801000 | -4.055067000 | 0.926225000 |
| H | -3.602740000 | -1.081474000 | -2.215020000 |
| H | -4.694415000 | -2.971188000 | -0.977747000 |
| H | -1.286360000 | -3.301806000 | 1.651715000 |
| H | -0.589186000 | -0.413142000 | -2.428718000 |
| H | -0.745639000 | 1.849648000 | -2.144062000 |
| H | -2.412865000 | 1.239756000 | -2.321790000 |
| H | -1.082382000 | 2.170058000 | 0.329328000 |
| H | 2.646272000 | -0.652106000 | 2.359739000 |
| H | 0.890398000 | -1.772311000 | 2.984333000 |
| H | 2.303888000 | -2.658639000 | 1.625437000 |
| H | 3.352276000 | 2.936969000 | 0.183586000 |
| H | 3.288217000 | -1.232794000 | -0.899941000 |
| H | 5.842537000 | 2.890139000 | 0.212788000 |
| H | 5.770504000 | -1.293499000 | -0.834253000 |
| H | 7.074833000 | 0.769405000 | -0.285593000 |
| H | -4.917745000 | 1.337892000 | -0.124512000 |
| C | -4.147703000 | 3.648340000 | 1.479102000 |
| H | -4.356346000 | 3.792306000 | 2.547358000 |
| H | -3.538639000 | 4.491290000 | 1.108731000 |
| H | -5.099333000 | 3.627322000 | 0.921725000 |

**22-ester:** E= -1370.452624

| | | | |
|---|---|---|---|
| C | -3.007667000 | -1.763784000 | 0.321123000 |
| C | -2.907032000 | -0.561635000 | -0.390441000 |
| C | -4.049031000 | 0.227374000 | -0.595873000 |
| C | -5.282421000 | -0.196050000 | -0.094059000 |
| C | -5.391632000 | -1.399653000 | 0.609157000 |
| C | -4.247451000 | -2.177116000 | 0.813891000 |
| O | -1.695659000 | -0.179780000 | -0.903071000 |
| Pd | 0.475750000 | -0.378451000 | -0.158352000 |
| P | 0.636084000 | -2.677496000 | -0.721623000 |
| C | 2.412113000 | -0.382816000 | 0.340509000 |
| C | 3.299980000 | 0.490279000 | -0.337463000 |
| C | 4.684816000 | 0.376196000 | -0.081982000 |
| C | 5.178406000 | -0.542201000 | 0.844512000 |
| C | 4.300057000 | -1.363407000 | 1.553768000 |

| | | | |
|---|---|---|---|
| C | 2.924775000 | -1.274737000 | 1.290526000 |
| N | 2.850327000 | 1.423250000 | -1.265086000 |
| C | 1.562191000 | 2.114225000 | -1.191449000 |
| C | 0.749470000 | 1.734547000 | 0.042869000 |
| C | -0.586944000 | 2.338267000 | 0.088270000 |
| O | -1.402591000 | 2.366293000 | -0.843300000 |
| O | -0.901524000 | 2.858367000 | 1.285310000 |
| H | 1.287992000 | 1.962032000 | 0.969267000 |
| H | 2.242421000 | -1.925357000 | 1.845793000 |
| H | 3.590423000 | 1.992447000 | -1.656507000 |
| H | 0.840102000 | -3.672844000 | 0.272877000 |
| H | -0.374077000 | -3.354613000 | -1.460307000 |
| H | 1.739954000 | -3.012754000 | -1.545169000 |
| H | 4.672156000 | -2.067223000 | 2.302518000 |
| H | 6.255861000 | -0.601001000 | 1.021663000 |
| H | 5.377915000 | 1.033233000 | -0.618246000 |
| H | 1.769462000 | 3.204607000 | -1.175725000 |
| H | 0.960275000 | 1.934167000 | -2.100468000 |
| H | -2.110454000 | -2.359415000 | 0.496162000 |
| H | -3.958942000 | 1.167513000 | -1.144706000 |
| H | -4.315709000 | -3.116048000 | 1.369474000 |
| H | -6.167139000 | 0.424483000 | -0.259252000 |
| H | -6.358560000 | -1.726827000 | 0.997807000 |
| H | -1.700682000 | 0.794071000 | -1.133149000 |
| C | -2.218976000 | 3.383007000 | 1.447378000 |
| H | -2.259240000 | 3.787679000 | 2.466362000 |
| H | -2.419902000 | 4.177654000 | 0.713453000 |
| H | -2.975641000 | 2.592606000 | 1.326332000 |

**18-ester:** E= -1063.273047

| | | | |
|---|---|---|---|
| Pd | -0.085613000 | -0.863577000 | -0.049758000 |
| C | -2.109056000 | 1.163339000 | 0.033899000 |
| O | -2.735890000 | 1.125820000 | 1.235528000 |
| C | 1.771824000 | -0.184141000 | 0.196855000 |
| C | 2.310070000 | 1.066410000 | -0.178524000 |
| C | 3.713890000 | 1.228757000 | -0.150210000 |
| C | 4.549951000 | 0.194958000 | 0.269028000 |
| C | 4.016509000 | -1.033221000 | 0.671443000 |
| C | 2.625546000 | -1.204136000 | 0.636199000 |
| N | 1.501279000 | 2.134770000 | -0.532018000 |
| C | 0.095091000 | 1.994648000 | -0.847196000 |
| C | -0.626348000 | 1.139949000 | 0.183769000 |
| P | -2.140641000 | -2.063436000 | -0.574023000 |
| O | -2.725207000 | 1.216127000 | -1.011778000 |
| H | 2.206241000 | -2.166854000 | 0.958028000 |
| H | 1.974416000 | 2.899256000 | -0.997534000 |
| H | -2.744874000 | -1.837347000 | -1.837185000 |
| H | -2.114465000 | -3.485134000 | -0.632362000 |
| H | -3.316501000 | -1.950843000 | 0.215896000 |
| H | 4.665967000 | -1.842590000 | 1.013340000 |
| H | 5.631558000 | 0.355119000 | 0.285608000 |
| H | 4.144852000 | 2.187261000 | -0.458053000 |
| H | -0.338535000 | 3.012584000 | -0.834992000 |
| H | -0.091387000 | 1.594238000 | -1.864409000 |
| H | -0.343697000 | 1.424436000 | 1.205015000 |
| C | -4.158500000 | 1.174429000 | 1.208698000 |
| H | -4.486916000 | 1.149805000 | 2.255492000 |
| H | -4.513691000 | 2.094945000 | 0.720145000 |
| H | -4.579199000 | 0.316271000 | 0.660585000 |

**TS3-ester:** E= -1063.255689

| | | | |
|---|---|---|---|
| Pd | 0.318070000 | 0.852286000 | -0.123950000 |
| C | 1.636697000 | -1.427052000 | 0.126642000 |
| O | 2.004244000 | -1.441599000 | 1.433841000 |
| C | -1.425819000 | -0.089045000 | 0.339171000 |
| C | -2.308148000 | -0.700172000 | -0.586899000 |
| C | -3.688473000 | -0.438134000 | -0.480900000 |
| C | -4.175246000 | 0.312292000 | 0.591711000 |
| C | -3.315094000 | 0.799041000 | 1.582404000 |
| C | -1.934740000 | 0.576203000 | 1.465646000 |
| N | -1.761575000 | -1.589112000 | -1.475350000 |
| C | -0.338444000 | -1.850491000 | -1.392882000 |
| C | 0.143598000 | -1.402494000 | -0.019642000 |
| P | 2.126084000 | 2.199695000 | -0.710390000 |
| O | 2.440873000 | -1.539939000 | -0.777511000 |
| H | -1.258209000 | 0.948052000 | 2.240153000 |
| H | -2.294769000 | -1.916572000 | -2.268947000 |
| H | 2.644378000 | 2.122071000 | -2.031900000 |
| H | 2.042102000 | 3.620499000 | -0.654910000 |
| H | 3.378253000 | 2.096021000 | -0.041762000 |
| H | -3.709180000 | 1.349518000 | 2.439784000 |
| H | -5.251053000 | 0.491568000 | 0.669854000 |
| H | -4.377663000 | -0.864197000 | -1.215847000 |
| H | -0.150650000 | -2.932549000 | -1.528448000 |
| H | 0.245287000 | -1.325575000 | -2.171610000 |
| H | -0.283493000 | -1.995403000 | 0.796806000 |
| C | 3.402180000 | -1.495859000 | 1.690631000 |
| H | 3.511975000 | -1.578111000 | 2.779594000 |
| H | 3.864740000 | -2.362029000 | 1.193441000 |
| H | 3.906821000 | -0.583541000 | 1.332878000 |

**3M-ester:** E= -592.306459

| | | | |
|---|---|---|---|
| C | -0.524311000 | 1.839288000 | -0.895436000 |
| N | 0.532279000 | 2.011102000 | 0.104816000 |
| C | 1.324022000 | 0.874185000 | 0.149476000 |
| C | 0.707263000 | -0.190019000 | -0.537948000 |
| C | -0.621460000 | 0.302642000 | -1.105063000 |
| C | 1.291194000 | -1.449153000 | -0.580917000 |
| C | 2.530001000 | -1.647991000 | 0.050685000 |
| C | 3.149789000 | -0.585666000 | 0.718200000 |
| C | 2.559734000 | 0.683992000 | 0.780285000 |
| C | -1.769745000 | -0.412161000 | -0.400105000 |
| O | -2.205155000 | 0.243766000 | 0.688451000 |
| O | -2.210365000 | -1.477553000 | -0.757104000 |
| H | 0.790329000 | -2.269502000 | -1.101653000 |
| H | 0.972054000 | 2.919948000 | 0.187957000 |
| H | 3.008982000 | -2.629075000 | 0.018809000 |
| H | 4.116315000 | -0.745083000 | 1.204242000 |
| H | 3.051665000 | 1.503164000 | 1.310709000 |
| H | -1.475253000 | 2.271001000 | -0.551560000 |
| H | -0.255837000 | 2.320894000 | -1.855607000 |
| H | -0.728498000 | 0.040329000 | -2.167751000 |
| C | -3.221074000 | -0.404240000 | 1.454628000 |
| H | -3.451442000 | 0.269369000 | 2.289190000 |
| H | -4.119868000 | -0.580482000 | 0.844531000 |
| H | -2.862734000 | -1.373246000 | 1.833816000 |

**14-enol-ester-I:** E= -1361.731166

| | | | |
|---|---|---|---|
| C | -0.161540000 | 2.493110000 | 0.040451000 |
| C | -1.898487000 | -0.743216000 | -0.181640000 |
| C | -2.751045000 | 0.072676000 | 0.611074000 |
| N | -2.328486000 | 0.999758000 | 1.565669000 |
| C | -1.008252000 | 1.227942000 | 2.095070000 |
| C | -0.309489000 | 2.480464000 | 1.540248000 |
| C | -4.150062000 | -0.029331000 | 0.414698000 |
| C | -4.702044000 | -0.884410000 | -0.533839000 |
| C | -3.868357000 | -1.680777000 | -1.321171000 |
| C | -2.484926000 | -1.601479000 | -1.125071000 |
| Pd | 0.138609000 | -0.578347000 | -0.140291000 |
| P | 0.382529000 | -2.733299000 | 0.376354000 |
| O | -0.074073000 | 1.506103000 | -0.679677000 |
| O | -0.106789000 | 3.714134000 | -0.464915000 |
| I | 2.874558000 | -0.338048000 | -0.025929000 |
| H | -4.281614000 | -2.355025000 | -2.075252000 |
| H | -3.081168000 | 1.479834000 | 2.041049000 |
| H | -4.811003000 | 0.592252000 | 1.028953000 |
| H | -5.788091000 | -0.927102000 | -0.652670000 |
| H | -1.840859000 | -2.227915000 | -1.750025000 |
| H | -1.059633000 | 1.335003000 | 3.192624000 |
| H | -0.376813000 | 0.341983000 | 1.910054000 |
| H | -0.837493000 | 3.400592000 | 1.833108000 |
| H | 0.712091000 | 2.554275000 | 1.957412000 |
| H | 0.909654000 | -3.029524000 | 1.655573000 |
| H | -0.755809000 | -3.581149000 | 0.378810000 |
| H | 1.259126000 | -3.498915000 | -0.427759000 |
| C | 0.119159000 | 3.837799000 | -1.879114000 |
| H | 0.161985000 | 4.914505000 | -2.079449000 |
| H | 1.064870000 | 3.351853000 | -2.157859000 |
| H | -0.704231000 | 3.372420000 | -2.439449000 |

**TS1-ester-I:** E= -1361.693375

| | | | |
|---|---|---|---|
| C | -1.346206000 | 1.803296000 | 0.163102000 |
| C | -1.722893000 | -0.146462000 | -0.209577000 |
| C | -2.489704000 | -0.776170000 | 0.820611000 |
| N | -2.269766000 | -0.454557000 | 2.132571000 |
| C | -1.572637000 | 0.770975000 | 2.489888000 |
| C | -1.944979000 | 1.927192000 | 1.563660000 |
| C | -3.485382000 | -1.723834000 | 0.475402000 |
| C | -3.741095000 | -2.022547000 | -0.855062000 |
| C | -3.030365000 | -1.382756000 | -1.888598000 |
| C | -2.046144000 | -0.460979000 | -1.555126000 |
| Pd | 0.418652000 | -0.134024000 | -0.052697000 |
| P | 0.748350000 | -2.370869000 | -0.115173000 |
| O | -0.060966000 | 1.858072000 | 0.036623000 |
| O | -2.099428000 | 2.516560000 | -0.720888000 |
| I | 3.098301000 | 0.084684000 | -0.001418000 |
| H | -3.249181000 | -1.610726000 | -2.934138000 |
| H | -2.926021000 | -0.827438000 | 2.806936000 |
| H | -4.062334000 | -2.208124000 | 1.269448000 |
| H | -4.516546000 | -2.753996000 | -1.099092000 |
| H | -1.488495000 | 0.028657000 | -2.357777000 |
| H | -1.829506000 | 1.017303000 | 3.530062000 |
| H | -0.477324000 | 0.621143000 | 2.454937000 |
| H | -3.037413000 | 2.027311000 | 1.483666000 |
| H | -1.542495000 | 2.868644000 | 1.972481000 |
| H | 1.456988000 | -2.979711000 | 0.947487000 |

| | | | |
|---|---|---|---|
| H | -0.394883000 | -3.216298000 | -0.150994000 |
| H | 1.465026000 | -2.906406000 | -1.211630000 |
| C | -1.455887000 | 3.003396000 | -1.892683000 |
| H | -2.232848000 | 3.524029000 | -2.467862000 |
| H | -0.641626000 | 3.698525000 | -1.638957000 |
| H | -1.033249000 | 2.189142000 | -2.501346000 |

**15-ester-I:** E= -1361.713047

| | | | |
|---|---|---|---|
| C | 1.658279000 | -1.447552000 | -0.189351000 |
| C | 1.889241000 | 0.093234000 | -0.241191000 |
| C | 2.327417000 | 0.788563000 | 0.943557000 |
| N | 2.440349000 | 0.127196000 | 2.123571000 |
| C | 2.106759000 | -1.282275000 | 2.282953000 |
| C | 2.431481000 | -2.045671000 | 1.005984000 |
| C | 2.683626000 | 2.156027000 | 0.831609000 |
| C | 2.682869000 | 2.791671000 | -0.404594000 |
| C | 2.303257000 | 2.115008000 | -1.575761000 |
| C | 1.916224000 | 0.779959000 | -1.486031000 |
| Pd | -0.386626000 | 0.228472000 | -0.145124000 |
| P | -1.115398000 | 2.392966000 | -0.220787000 |
| O | 0.312158000 | -1.651554000 | -0.040624000 |
| O | 2.165376000 | -1.956286000 | -1.416466000 |
| I | -2.943317000 | -0.426342000 | 0.185330000 |
| H | 2.325712000 | 2.620720000 | -2.542868000 |
| H | 2.648776000 | 0.671473000 | 2.950982000 |
| H | 3.011744000 | 2.692865000 | 1.726038000 |
| H | 2.997687000 | 3.837645000 | -0.460382000 |
| H | 1.678574000 | 0.199190000 | -2.378281000 |
| H | 2.685403000 | -1.676032000 | 3.132884000 |
| H | 1.033479000 | -1.406887000 | 2.517477000 |
| H | 3.512658000 | -2.003669000 | 0.794480000 |
| H | 2.135064000 | -3.097726000 | 1.125618000 |
| H | -1.846931000 | 2.915060000 | 0.872902000 |
| H | -0.129152000 | 3.409506000 | -0.358940000 |
| H | -1.984195000 | 2.767040000 | -1.274323000 |
| C | 1.759296000 | -3.266808000 | -1.758120000 |
| H | 2.145839000 | -3.463006000 | -2.768854000 |
| H | 2.181064000 | -4.028740000 | -1.074777000 |
| H | 0.662384000 | -3.366063000 | -1.759527000 |

**16-enol-ester-I:** E= -1361.733589

| | | | |
|---|---|---|---|
| C | -0.466310000 | 3.530136000 | 0.749612000 |
| C | -0.334705000 | 2.290398000 | 0.121647000 |
| C | 0.693680000 | 2.105745000 | -0.805034000 |
| C | 1.609356000 | 3.099981000 | -1.140816000 |
| C | 1.467341000 | 4.342514000 | -0.505039000 |
| C | 0.441556000 | 4.552086000 | 0.425437000 |
| Pd | -1.093402000 | 0.426497000 | 0.029354000 |
| P | -2.782228000 | 0.567773000 | 1.500195000 |
| N | 0.614779000 | 0.736300000 | -1.327891000 |
| C | 1.827151000 | -0.108975000 | -1.283209000 |
| C | 2.278998000 | -0.406085000 | 0.139872000 |
| C | 3.563167000 | -1.206621000 | 0.165379000 |
| O | 3.884627000 | -1.565998000 | 1.419323000 |
| I | -1.746059000 | -2.174434000 | -0.416793000 |
| O | 4.229264000 | -1.488987000 | -0.801689000 |
| H | 0.347176000 | 5.529441000 | 0.907427000 |
| H | 2.407592000 | 2.929903000 | -1.868477000 |
| H | 2.161545000 | 5.153231000 | -0.739622000 |

| | | | |
|---|---|---|---|
| H | -1.254269000 | 3.723908000 | 1.483712000 |
| H | 0.248852000 | 0.735948000 | -2.281302000 |
| H | 1.584153000 | -1.050308000 | -1.796890000 |
| H | 2.649297000 | 0.365307000 | -1.846050000 |
| H | 2.448334000 | 0.521940000 | 0.711930000 |
| H | 1.501968000 | -0.964959000 | 0.687439000 |
| H | -2.756980000 | -0.306524000 | 2.612404000 |
| H | -3.019283000 | 1.795360000 | 2.176223000 |
| H | -4.088469000 | 0.312476000 | 1.020249000 |
| C | 5.081957000 | -2.329068000 | 1.574171000 |
| H | 5.180070000 | -2.529124000 | 2.648205000 |
| H | 5.018002000 | -3.274544000 | 1.014611000 |
| H | 5.955323000 | -1.767417000 | 1.209017000 |

**17-ester-I:** E= -1361.206383

| | | | |
|---|---|---|---|
| C | -2.410347000 | -0.497681000 | 1.042027000 |
| C | -1.559885000 | -0.919962000 | -0.017121000 |
| C | -2.107097000 | -1.770848000 | -0.988343000 |
| N | -1.982509000 | 0.365567000 | 2.041123000 |
| C | -0.330150000 | 1.540652000 | 0.512984000 |
| Pd | 0.395167000 | -0.367784000 | -0.049589000 |
| I | 3.142498000 | 0.362102000 | 0.082111000 |
| P | 1.236608000 | -2.518539000 | -0.445192000 |
| C | -3.427981000 | -2.247579000 | -0.932229000 |
| C | -4.235124000 | -1.866323000 | 0.140495000 |
| C | -3.731562000 | -0.998491000 | 1.110554000 |
| H | -1.481909000 | -2.090320000 | -1.828757000 |
| H | -2.733414000 | 0.640283000 | 2.662032000 |
| H | 0.385460000 | -3.640774000 | -0.699742000 |
| H | 2.160085000 | -2.766294000 | -1.498501000 |
| H | 2.001379000 | -3.123045000 | 0.588845000 |
| H | -3.809557000 | -2.911099000 | -1.714543000 |
| H | -5.264470000 | -2.231008000 | 0.222395000 |
| H | -4.374146000 | -0.682464000 | 1.941509000 |
| C | -0.970752000 | 1.419410000 | 1.884277000 |
| H | -1.458502000 | 2.376411000 | 2.164835000 |
| H | -0.154929000 | 1.259267000 | 2.613140000 |
| H | 0.628982000 | 2.068415000 | 0.573742000 |
| C | -1.127280000 | 2.161973000 | -0.569085000 |
| O | -0.711355000 | 2.611382000 | -1.618474000 |
| O | -2.468945000 | 2.214747000 | -0.277771000 |
| C | -3.307244000 | 2.683572000 | -1.314825000 |
| H | -3.054108000 | 3.716652000 | -1.607283000 |
| H | -3.223824000 | 2.049853000 | -2.212830000 |
| H | -4.335769000 | 2.642546000 | -0.928065000 |

**TS2-ester-I:** E= -1361.170592

| | | | |
|---|---|---|---|
| C | 2.199676000 | 0.842218000 | 1.117428000 |
| C | 1.471142000 | 0.606313000 | -0.085996000 |
| C | 2.027190000 | 1.095380000 | -1.287327000 |
| N | 1.770594000 | 0.096733000 | 2.213004000 |
| C | 0.912180000 | -1.192165000 | 0.304707000 |
| Pd | -0.616422000 | 0.484598000 | -0.122462000 |
| I | -3.209918000 | -0.785836000 | 0.026195000 |
| P | -1.466399000 | 2.640979000 | -0.274541000 |
| C | 3.136020000 | 1.955470000 | -1.272351000 |
| C | 3.752768000 | 2.290785000 | -0.062973000 |
| C | 3.295964000 | 1.710809000 | 1.131833000 |
| H | 1.561336000 | 0.827448000 | -2.238944000 |

| | | | |
|---|---|---|---|
| H | 2.468346000 | -0.014458000 | 2.940020000 |
| H | -0.719540000 | 3.863600000 | -0.385125000 |
| H | -2.369262000 | 2.957890000 | -1.334181000 |
| H | -2.324275000 | 3.115914000 | 0.762328000 |
| H | 3.511359000 | 2.366634000 | -2.214867000 |
| H | 4.610903000 | 2.969367000 | -0.045398000 |
| H | 3.819754000 | 1.902580000 | 2.075079000 |
| C | 1.081702000 | -1.151000000 | 1.822563000 |
| H | 1.662267000 | -2.021668000 | 2.174167000 |
| H | 0.082337000 | -1.195826000 | 2.285836000 |
| H | -0.071548000 | -1.606020000 | 0.010642000 |
| C | 1.924548000 | -1.891494000 | -0.522799000 |
| O | 1.802758000 | -2.203527000 | -1.687587000 |
| O | 3.076567000 | -2.143824000 | 0.166119000 |
| C | 4.129367000 | -2.719104000 | -0.587903000 |
| H | 3.838670000 | -3.697657000 | -1.004196000 |
| H | 4.418078000 | -2.065753000 | -1.426481000 |
| H | 4.976538000 | -2.840571000 | 0.101758000 |

**18-ester-I:** E= -1063.272072

| | | | |
|---|---|---|---|
| C | 0.607787000 | 1.821981000 | -0.587947000 |
| C | 0.942877000 | 0.642294000 | 0.120281000 |
| C | 1.857339000 | 0.701071000 | 1.179871000 |
| N | -0.294514000 | 1.884145000 | -1.625070000 |
| C | -1.494931000 | -0.210163000 | -0.997189000 |
| Pd | 0.204582000 | -1.171759000 | -0.323325000 |
| P | 2.164869000 | -2.508947000 | 0.102745000 |
| C | 2.474566000 | 1.898686000 | 1.559179000 |
| C | 2.171661000 | 3.061912000 | 0.845861000 |
| C | 1.263286000 | 3.021472000 | -0.204841000 |
| H | 2.086612000 | -0.201963000 | 1.752523000 |
| H | -0.579377000 | 2.820005000 | -1.878220000 |
| H | 2.584161000 | -2.894703000 | 1.406672000 |
| H | 2.285218000 | -3.793389000 | -0.498008000 |
| H | 3.405830000 | -1.983097000 | -0.340179000 |
| H | 3.171726000 | 1.915916000 | 2.400099000 |
| H | 2.643245000 | 4.012070000 | 1.110988000 |
| H | 1.033549000 | 3.936984000 | -0.759324000 |
| C | -1.190191000 | 0.825752000 | -2.057918000 |
| H | -2.122568000 | 1.319001000 | -2.388295000 |
| H | -0.779672000 | 0.300396000 | -2.943173000 |
| H | -1.938257000 | -1.119698000 | -1.447020000 |
| C | -2.359000000 | 0.269114000 | 0.117110000 |
| O | -2.637604000 | 1.422056000 | 0.361162000 |
| O | -2.836067000 | -0.764902000 | 0.863035000 |
| C | -3.648000000 | -0.406854000 | 1.975683000 |
| H | -3.083925000 | 0.206069000 | 2.696292000 |
| H | -4.530869000 | 0.167912000 | 1.654762000 |
| H | -3.960885000 | -1.348226000 | 2.446021000 |

**TS3-ester-I:** E= -1063.256912

| | | | |
|---|---|---|---|
| C | 0.867954000 | 1.621232000 | 0.788786000 |
| C | 0.294498000 | 0.759942000 | -0.172258000 |
| C | 0.411682000 | 1.046524000 | -1.537825000 |
| N | 0.911626000 | 1.186984000 | 2.097466000 |
| C | 0.601682000 | -0.979072000 | 0.978041000 |
| Pd | -1.325065000 | -0.482148000 | 0.181579000 |
| P | -3.535849000 | -0.074929000 | -0.437472000 |
| C | 0.957315000 | 2.269606000 | -1.954067000 |

| | | | |
|---|---|---|---|
| C | 1.422045000 | 3.176952000 | -0.996240000 |
| C | 1.391729000 | 2.857011000 | 0.362131000 |
| H | 0.057872000 | 0.328635000 | -2.281299000 |
| H | 1.535427000 | 1.698624000 | 2.709809000 |
| H | -3.844520000 | 0.168029000 | -1.803972000 |
| H | -4.594839000 | -0.997762000 | -0.198849000 |
| H | -4.199715000 | 1.066276000 | 0.089347000 |
| H | 1.015480000 | 2.505784000 | -3.019292000 |
| H | 1.845155000 | 4.134888000 | -1.310407000 |
| H | 1.809955000 | 3.546931000 | 1.100943000 |
| C | 0.872275000 | -0.266175000 | 2.296547000 |
| H | 1.841075000 | -0.612381000 | 2.698630000 |
| H | 0.084294000 | -0.529549000 | 3.020893000 |
| H | -0.032324000 | -1.888687000 | 1.118068000 |
| C | 1.824863000 | -1.388109000 | 0.218396000 |
| O | 2.962994000 | -1.144087000 | 0.549520000 |
| O | 1.516714000 | -2.102091000 | -0.885278000 |
| C | 2.618450000 | -2.523311000 | -1.686147000 |
| H | 3.177977000 | -1.655729000 | -2.068372000 |
| H | 3.309977000 | -3.154307000 | -1.106929000 |
| H | 2.190916000 | -3.095065000 | -2.519514000 |

**14-xant-A:** E= -2212.005948

| | | | |
|---|---|---|---|
| C | 0.751275000 | -2.224303000 | 2.014611000 |
| C | 1.552527000 | -2.110980000 | 0.865397000 |
| C | 2.306885000 | -3.249157000 | 0.467266000 |
| C | 2.213061000 | -4.431955000 | 1.238009000 |
| C | 1.418092000 | -4.506296000 | 2.378066000 |
| C | 0.678107000 | -3.393212000 | 2.780521000 |
| Pd | 1.713538000 | -0.317192000 | -0.060176000 |
| N | 3.185287000 | -3.290273000 | -0.622840000 |
| C | 3.292631000 | -2.366173000 | -1.725059000 |
| C | 4.572183000 | -1.514674000 | -1.694228000 |
| C | 4.774365000 | -0.682076000 | -0.446819000 |
| O | 3.851168000 | -0.317196000 | 0.270487000 |
| H | 0.048295000 | -3.429949000 | 3.672857000 |
| C | 6.183507000 | -0.296303000 | -0.087479000 |
| P | -0.494562000 | -0.228774000 | -0.437793000 |
| H | 3.587029000 | -4.204104000 | -0.787183000 |
| H | 2.790646000 | -5.309296000 | 0.925430000 |
| H | 1.376024000 | -5.439412000 | 2.946493000 |
| H | 0.165151000 | -1.359386000 | 2.340968000 |
| H | 3.280240000 | -2.915867000 | -2.683059000 |
| H | 2.407521000 | -1.707345000 | -1.747992000 |
| H | 5.464435000 | -2.149396000 | -1.829220000 |
| H | 4.576454000 | -0.804912000 | -2.544719000 |
| H | 6.180710000 | 0.504908000 | 0.662177000 |
| H | 6.696598000 | -1.182100000 | 0.326230000 |
| H | 6.745213000 | 0.014572000 | -0.982348000 |
| H | -0.797327000 | -0.005268000 | -1.804137000 |
| H | -1.265611000 | -1.392082000 | -0.208956000 |
| O | 1.873599000 | 1.457404000 | -1.162265000 |
| C | 2.372132000 | 2.604061000 | -0.745718000 |
| C | 2.435045000 | 3.702787000 | -1.647145000 |
| C | 2.862543000 | 2.827416000 | 0.569385000 |
| C | 2.949890000 | 4.935472000 | -1.253288000 |
| C | 3.374354000 | 4.070742000 | 0.951313000 |
| C | 3.425905000 | 5.138599000 | 0.049986000 |
| H | 2.061376000 | 3.548611000 | -2.662917000 |
| H | 2.846548000 | 2.000514000 | 1.285016000 |
| H | 2.979214000 | 5.757073000 | -1.976385000 |

| | | | |
|---|---|---|---|
| H | 3.741171000 | 4.203119000 | 1.974461000 |
| H | 3.826791000 | 6.108660000 | 0.353864000 |
| C | -1.455314000 | 1.069923000 | 0.422866000 |
| C | -0.804268000 | 2.045110000 | 1.188481000 |
| C | -2.860672000 | 1.111117000 | 0.319045000 |
| C | -1.542720000 | 3.028450000 | 1.851988000 |
| H | 0.284750000 | 2.038009000 | 1.258273000 |
| C | -3.616201000 | 2.092871000 | 0.972556000 |
| C | -2.933011000 | 3.042490000 | 1.744200000 |
| H | -1.026731000 | 3.785505000 | 2.445763000 |
| C | -4.809700000 | -0.052983000 | -0.416495000 |
| H | -3.511877000 | 3.813718000 | 2.260906000 |
| C | -5.669157000 | 0.861082000 | 0.204351000 |
| C | -5.275257000 | -1.225813000 | -1.038477000 |
| C | -7.038968000 | 0.566753000 | 0.220327000 |
| C | -6.653376000 | -1.478835000 | -1.010376000 |
| C | -7.531630000 | -0.592070000 | -0.379924000 |
| H | -7.725035000 | 1.265841000 | 0.706983000 |
| H | -7.045065000 | -2.381831000 | -1.485252000 |
| H | -8.602942000 | -0.805264000 | -0.363412000 |
| O | -3.447685000 | 0.147807000 | -0.459896000 |
| C | -5.117996000 | 2.135184000 | 0.802551000 |
| H | -5.389294000 | 2.991481000 | 0.154695000 |
| H | -5.601531000 | 2.335383000 | 1.773799000 |
| P | -4.039160000 | -2.424538000 | -1.716865000 |
| H | -4.967813000 | -3.167813000 | -2.506455000 |
| H | -3.580927000 | -1.638449000 | -2.820127000 |

**TS1-xant-A:** E= -2211.977956

| | | | |
|---|---|---|---|
| C | 1.831242000 | -1.806228000 | 2.093916000 |
| C | 2.143453000 | -1.963266000 | 0.719610000 |
| C | 1.798192000 | -3.200736000 | 0.098537000 |
| C | 1.099968000 | -4.187790000 | 0.839639000 |
| C | 0.778551000 | -3.971050000 | 2.170761000 |
| C | 1.153761000 | -2.777344000 | 2.818449000 |
| Pd | 1.954732000 | -0.132197000 | -0.312575000 |
| N | 2.150057000 | -3.441479000 | -1.206317000 |
| C | 3.231493000 | -2.695958000 | -1.823103000 |
| C | 4.405134000 | -2.492376000 | -0.852829000 |
| C | 4.146847000 | -1.465472000 | 0.251799000 |
| O | 4.006722000 | -0.236453000 | -0.111072000 |
| H | 0.911195000 | -2.620137000 | 3.871808000 |
| C | 4.884701000 | -1.712294000 | 1.555283000 |
| P | -0.308538000 | -0.164274000 | -0.505098000 |
| H | 2.010121000 | -4.389427000 | -1.534106000 |
| H | 0.825730000 | -5.129231000 | 0.353507000 |
| H | 0.242328000 | -4.746332000 | 2.724938000 |
| H | 2.122783000 | -0.876025000 | 2.591462000 |
| H | 3.558289000 | -3.245458000 | -2.717753000 |
| H | 2.879903000 | -1.703889000 | -2.163082000 |
| H | 4.694713000 | -3.462303000 | -0.418461000 |
| H | 5.268151000 | -2.101791000 | -1.418417000 |
| H | 4.590377000 | -0.971866000 | 2.309604000 |
| H | 4.727877000 | -2.728384000 | 1.942452000 |
| H | 5.963061000 | -1.575771000 | 1.355513000 |
| H | -0.750316000 | -0.008406000 | -1.842219000 |
| H | -0.997228000 | -1.359056000 | -0.176751000 |
| O | 1.756913000 | 1.628601000 | -1.363087000 |
| C | 2.227537000 | 2.801849000 | -0.971333000 |
| C | 1.925164000 | 3.950428000 | -1.750193000 |
| C | 3.013899000 | 2.996739000 | 0.192393000 |

```
C        2.376880000      5.214067000     -1.376418000
C        3.457329000      4.271166000      0.555843000
C        3.145227000      5.393375000     -0.217943000
H        1.323531000      3.812025000     -2.652089000
H        3.293679000      2.125183000      0.789447000
H        2.123619000      6.077130000     -2.000468000
H        4.065380000      4.384270000      1.459156000
H        3.496604000      6.386950000      0.070994000
C       -1.267719000      1.104566000      0.401286000
C       -0.608884000      2.112504000      1.116150000
C       -2.677271000      1.093742000      0.382339000
C       -1.342343000      3.075834000      1.814029000
H        0.481710000      2.150825000      1.117084000
C       -3.428493000      2.055143000      1.070030000
C       -2.735857000      3.038438000      1.789530000
H       -0.820013000      3.859789000      2.365913000
C       -4.626985000     -0.126446000     -0.259296000
H       -3.311017000      3.795175000      2.331282000
C       -5.482181000      0.765254000      0.399127000
C       -5.093107000     -1.302348000     -0.875987000
C       -6.845129000      0.445010000      0.457720000
C       -6.464245000     -1.582077000     -0.803634000
C       -7.336997000     -0.717329000     -0.136033000
H       -7.527019000      1.127492000      0.973040000
H       -6.855105000     -2.487603000     -1.274446000
H       -8.403225000     -0.949938000     -0.086244000
O       -3.272500000      0.098746000     -0.350305000
C       -4.938499000      2.044005000      0.993890000
H       -5.281108000      2.904551000      0.387162000
H       -5.366988000      2.203215000      1.998382000
P       -3.861678000     -2.471080000     -1.612100000
H       -4.802297000     -3.207686000     -2.394098000
H       -3.438673000     -1.657153000     -2.708615000
```

**15-xant-A:** E= -1514.236638

```
symmetry c1
C        1.192793000     -2.145745000      1.878693000
C        2.195404000     -2.202590000      0.869178000
C        1.913747000     -2.987067000     -0.310442000
C        0.658868000     -3.636919000     -0.420995000
C       -0.280376000     -3.557547000      0.599023000
C       -0.026652000     -2.809479000      1.758861000
Pd       1.684488000     -0.090117000      0.190729000
N        2.854190000     -3.132671000     -1.281210000
C        4.123790000     -2.425194000     -1.242145000
C        4.632603000     -2.388448000      0.191093000
C        3.641439000     -1.642385000      1.112434000
O        3.588190000     -0.293908000      0.750632000
H       -0.770394000     -2.745680000      2.555102000
C        4.090148000     -1.784861000      2.573735000
P       -0.529910000      0.086250000     -0.477851000
H        2.569475000     -3.574141000     -2.146218000
H        0.450718000     -4.232176000     -1.314599000
H       -1.234078000     -4.079387000      0.484887000
H        1.412497000     -1.593245000      2.793519000
H        4.831458000     -2.946601000     -1.904485000
H        4.012586000     -1.386460000     -1.608887000
H        4.796477000     -3.418838000      0.552556000
H        5.591638000     -1.850635000      0.231808000
H        3.458924000     -1.176321000      3.236798000
H        4.070884000     -2.832019000      2.917865000
```

| | | | |
|---|---|---|---|
| H | 5.118236000 | -1.401787000 | 2.665802000 |
| H | -0.744084000 | 0.297293000 | -1.866658000 |
| H | -1.353342000 | -1.053802000 | -0.310984000 |
| O | 1.849844000 | 1.854120000 | -0.426291000 |
| C | 3.052295000 | 2.344478000 | -0.722629000 |
| C | 3.440539000 | 2.513165000 | -2.073362000 |
| C | 3.945810000 | 2.776949000 | 0.285119000 |
| C | 4.655256000 | 3.116898000 | -2.398300000 |
| C | 5.159249000 | 3.376339000 | -0.049545000 |
| C | 5.523672000 | 3.553615000 | -1.390260000 |
| H | 2.754235000 | 2.173300000 | -2.853502000 |
| H | 3.660406000 | 2.624991000 | 1.327707000 |
| H | 4.929064000 | 3.249558000 | -3.449434000 |
| H | 5.833501000 | 3.708048000 | 0.745733000 |
| H | 6.476120000 | 4.024617000 | -1.646874000 |
| C | -1.540463000 | 1.414907000 | 0.285136000 |
| C | -0.895989000 | 2.467424000 | 0.950525000 |
| C | -2.948595000 | 1.407946000 | 0.221680000 |
| C | -1.646172000 | 3.479140000 | 1.556235000 |
| H | 0.196673000 | 2.489603000 | 0.963410000 |
| C | -3.714017000 | 2.418553000 | 0.818993000 |
| C | -3.038825000 | 3.445528000 | 1.491789000 |
| H | -1.139329000 | 4.296174000 | 2.074270000 |
| C | -4.888042000 | 0.143958000 | -0.363327000 |
| H | -3.626625000 | 4.238469000 | 1.963903000 |
| C | -5.755145000 | 1.082764000 | 0.208923000 |
| C | -5.343815000 | -1.082107000 | -0.882641000 |
| C | -7.116841000 | 0.761145000 | 0.282498000 |
| C | -6.714361000 | -1.362534000 | -0.800025000 |
| C | -7.597635000 | -0.449861000 | -0.215518000 |
| H | -7.806747000 | 1.480763000 | 0.732482000 |
| H | -7.096320000 | -2.306791000 | -1.196185000 |
| H | -8.663072000 | -0.683656000 | -0.155626000 |
| O | -3.534614000 | 0.369699000 | -0.459691000 |
| C | -5.220918000 | 2.410186000 | 0.694434000 |
| H | -5.535875000 | 3.209059000 | -0.005020000 |
| H | -5.681006000 | 2.669348000 | 1.663197000 |
| P | -4.104244000 | -2.306059000 | -1.504209000 |
| H | -5.030535000 | -3.097241000 | -2.248817000 |
| H | -3.648909000 | -1.580055000 | -2.648085000 |

**18-xant:** E= -1904.830269

| | | | |
|---|---|---|---|
| C | 5.312109000 | 1.885372000 | 0.356401000 |
| C | 4.683049000 | 1.171674000 | 1.375076000 |
| C | 3.487041000 | 0.455942000 | 1.138377000 |
| C | 2.889069000 | 0.514733000 | -0.143050000 |
| C | 3.562828000 | 1.209320000 | -1.157553000 |
| C | 4.767703000 | 1.890468000 | -0.929612000 |
| N | 2.915289000 | -0.268035000 | 2.175716000 |
| C | 2.155689000 | -1.500973000 | 1.995052000 |
| C | 2.044887000 | -1.974332000 | 0.548891000 |
| Pd | 1.095129000 | -0.390566000 | -0.560649000 |
| P | 0.286545000 | 1.757939000 | -1.298819000 |
| H | 3.030050000 | -2.086525000 | 0.077927000 |
| P | -0.832367000 | -1.673925000 | -1.418499000 |
| H | 3.141636000 | 1.234030000 | -2.168491000 |
| H | 3.452342000 | -0.244951000 | 3.033401000 |
| H | -0.193276000 | 1.928600000 | -2.631070000 |
| H | 1.231590000 | 2.812059000 | -1.295051000 |
| H | 5.264953000 | 2.419026000 | -1.747087000 |
| H | 6.240684000 | 2.423122000 | 0.567872000 |

| | | | |
|---|---|---|---|
| H | 5.128107000 | 1.144613000 | 2.375769000 |
| H | 2.656798000 | -2.289064000 | 2.596903000 |
| H | 1.146472000 | -1.389855000 | 2.433970000 |
| C | 1.301977000 | -3.246366000 | 0.346730000 |
| H | -0.680096000 | -3.074382000 | -1.577691000 |
| H | -1.147284000 | -1.349206000 | -2.767065000 |
| O | 1.498019000 | -3.974124000 | -0.618163000 |
| C | 0.253529000 | -3.659692000 | 1.381132000 |
| H | -0.299547000 | -4.528376000 | 0.998843000 |
| H | 0.748320000 | -3.949012000 | 2.323748000 |
| H | -0.442860000 | -2.842196000 | 1.625231000 |
| C | -1.074705000 | 2.560937000 | -0.352404000 |
| C | -0.962409000 | 3.746772000 | 0.387166000 |
| C | -2.283754000 | 1.862013000 | -0.277399000 |
| H | -0.034201000 | 4.322713000 | 0.359976000 |
| C | -2.031530000 | 4.181115000 | 1.179602000 |
| C | -3.362530000 | 2.255090000 | 0.519162000 |
| H | -1.934521000 | 5.103431000 | 1.756774000 |
| C | -3.215399000 | 3.437711000 | 1.254085000 |
| H | -4.034418000 | 3.779632000 | 1.892957000 |
| C | -2.503937000 | -1.613661000 | -0.641617000 |
| C | -3.193426000 | -2.704390000 | -0.092242000 |
| C | -3.046558000 | -0.339780000 | -0.442297000 |
| H | -2.809751000 | -3.718274000 | -0.227810000 |
| C | -4.359065000 | -2.492708000 | 0.654070000 |
| C | -4.183099000 | -0.088626000 | 0.330578000 |
| H | -4.888220000 | -3.347640000 | 1.081197000 |
| C | -4.838905000 | -1.197257000 | 0.879832000 |
| H | -5.732468000 | -1.045556000 | 1.491668000 |
| O | -2.358803000 | 0.704366000 | -1.014394000 |
| C | -4.590081000 | 1.361135000 | 0.525242000 |
| H | -5.270989000 | 1.666784000 | -0.293524000 |
| H | -5.157591000 | 1.484199000 | 1.460299000 |

**TS3-xant:** E= -1904.799724

| | | | |
|---|---|---|---|
| C | 5.021474000 | 2.112458000 | -0.772379000 |
| C | 4.567408000 | 1.968743000 | 0.545381000 |
| C | 3.632401000 | 0.970525000 | 0.855884000 |
| C | 3.080628000 | 0.175756000 | -0.175543000 |
| C | 3.624721000 | 0.255697000 | -1.465471000 |
| C | 4.573607000 | 1.244997000 | -1.772550000 |
| N | 3.225183000 | 0.640878000 | 2.137636000 |
| C | 2.686849000 | -0.712441000 | 2.290130000 |
| C | 2.743223000 | -1.445859000 | 0.946041000 |
| Pd | 1.073936000 | -0.416027000 | -0.350820000 |
| P | 0.207336000 | 1.839761000 | -0.783679000 |
| H | 3.763380000 | -1.740535000 | 0.676298000 |
| P | -0.666803000 | -1.857858000 | -1.207794000 |
| H | 3.291765000 | -0.436655000 | -2.243933000 |
| H | 3.781854000 | 1.002690000 | 2.901734000 |
| H | 0.069113000 | 2.129395000 | -2.172946000 |
| H | 1.016312000 | 2.968543000 | -0.474071000 |
| H | 4.964176000 | 1.324363000 | -2.790207000 |
| H | 5.758882000 | 2.885192000 | -1.005237000 |
| H | 4.967198000 | 2.604853000 | 1.341175000 |
| H | 3.274106000 | -1.266054000 | 3.048733000 |
| H | 1.649343000 | -0.673350000 | 2.660739000 |
| C | 1.922034000 | -2.700524000 | 0.789186000 |
| H | -0.458262000 | -3.265135000 | -1.229439000 |
| H | -0.841479000 | -1.691255000 | -2.611624000 |
| O | 2.232224000 | -3.564248000 | -0.022099000 |

| | | | |
|---|---|---|---|
| C | 0.798533000 | -2.984179000 | 1.789861000 |
| H | 0.182451000 | -3.806123000 | 1.400568000 |
| H | 1.246440000 | -3.323066000 | 2.740993000 |
| H | 0.166632000 | -2.112888000 | 2.012374000 |
| C | -1.405576000 | 2.489199000 | -0.160432000 |
| C | -1.560585000 | 3.691325000 | 0.547613000 |
| C | -2.532464000 | 1.663523000 | -0.283924000 |
| H | -0.707234000 | 4.363731000 | 0.666099000 |
| C | -2.792942000 | 4.026473000 | 1.118184000 |
| C | -3.773814000 | 1.963875000 | 0.287749000 |
| H | -2.897049000 | 4.963924000 | 1.669520000 |
| C | -3.888389000 | 3.164883000 | 0.997377000 |
| H | -4.844775000 | 3.427416000 | 1.458206000 |
| C | -2.430922000 | -1.849258000 | -0.662137000 |
| C | -3.136452000 | -2.982035000 | -0.228686000 |
| C | -3.069688000 | -0.606402000 | -0.547646000 |
| H | -2.674426000 | -3.969598000 | -0.303798000 |
| C | -4.418708000 | -2.853773000 | 0.316267000 |
| C | -4.343908000 | -0.444084000 | 0.007151000 |
| H | -4.954692000 | -3.743942000 | 0.653722000 |
| C | -5.013123000 | -1.593808000 | 0.442599000 |
| H | -6.009615000 | -1.500745000 | 0.883469000 |
| O | -2.366046000 | 0.491313000 | -0.984179000 |
| C | -4.897779000 | 0.964672000 | 0.093467000 |
| H | -5.442933000 | 1.202445000 | -0.841624000 |
| H | -5.635131000 | 1.044251000 | 0.907109000 |

**23-I:** E= -2203.294196

| | | | |
|---|---|---|---|
| C | -3.226176000 | -1.986915000 | 2.118668000 |
| C | -2.702237000 | -1.873079000 | 0.823353000 |
| C | -3.231268000 | -0.877852000 | -0.005956000 |
| C | -4.209425000 | 0.033421000 | 0.400557000 |
| C | -4.706455000 | -0.100874000 | 1.702689000 |
| C | -4.228805000 | -1.109318000 | 2.547725000 |
| C | -3.454817000 | 1.477149000 | -1.480800000 |
| C | -2.523487000 | 0.477531000 | -1.773294000 |
| C | -1.362851000 | 0.696082000 | -2.523420000 |
| C | -1.154527000 | 1.977985000 | -3.050371000 |
| C | -2.084326000 | 2.993888000 | -2.801058000 |
| C | -3.215377000 | 2.750127000 | -2.013078000 |
| H | -2.836389000 | -2.745262000 | 2.801641000 |
| H | -5.472026000 | 0.593113000 | 2.060660000 |
| H | -4.628885000 | -1.201996000 | 3.559920000 |
| H | -0.255517000 | 2.191797000 | -3.633124000 |
| H | -1.914088000 | 3.992263000 | -3.210017000 |
| H | -3.919595000 | 3.560660000 | -1.805841000 |
| P | -1.243743000 | -2.786457000 | 0.168563000 |
| H | -1.871004000 | -3.648703000 | -0.778660000 |
| H | -1.045568000 | -3.728096000 | 1.206213000 |
| P | -0.149731000 | -0.682440000 | -2.582623000 |
| H | -0.829883000 | -1.626465000 | -3.402639000 |
| H | 0.774207000 | -0.185806000 | -3.530666000 |
| Pd | 0.686120000 | -1.429303000 | -0.540183000 |
| C | 2.357966000 | -0.365806000 | -1.077848000 |
| C | 3.298916000 | -0.974388000 | -1.908290000 |
| C | 2.536276000 | 0.983415000 | -0.679862000 |
| C | 4.417483000 | -0.270044000 | -2.383456000 |
| H | 3.169673000 | -2.021343000 | -2.199938000 |
| C | 3.657487000 | 1.685676000 | -1.170333000 |
| C | 4.580700000 | 1.064983000 | -2.017463000 |
| H | 5.145379000 | -0.767572000 | -3.029496000 |

| | | | |
|---|---|---|---|
| H | 3.816263000 | 2.725786000 | -0.881353000 |
| H | 5.440682000 | 1.634974000 | -2.379914000 |
| I | 1.788363000 | -1.884397000 | 1.864478000 |
| N | 1.596566000 | 1.581840000 | 0.162708000 |
| H | 1.174359000 | 0.895529000 | 0.786080000 |
| C | 1.864098000 | 2.856543000 | 0.797421000 |
| H | 2.825970000 | 2.860719000 | 1.351253000 |
| H | 1.953825000 | 3.648477000 | 0.036722000 |
| C | 0.733979000 | 3.222775000 | 1.751734000 |
| H | -0.235891000 | 3.177373000 | 1.219980000 |
| H | 0.649979000 | 2.486918000 | 2.572312000 |
| C | 0.860002000 | 4.618869000 | 2.344689000 |
| O | 1.640450000 | 5.434206000 | 1.904326000 |
| C | -0.049576000 | 4.936694000 | 3.517792000 |
| H | -1.082658000 | 4.603747000 | 3.327496000 |
| H | 0.303569000 | 4.391226000 | 4.409946000 |
| H | -0.027961000 | 6.014516000 | 3.726241000 |
| C | -4.629506000 | 1.098512000 | -0.596687000 |
| H | -5.454029000 | 0.709546000 | -1.226063000 |
| H | -5.028305000 | 1.983318000 | -0.077614000 |
| O | -2.695343000 | -0.791135000 | -1.271368000 |

**23-OPh:** E= -2212.015906

| | | | |
|---|---|---|---|
| O | -2.876122000 | -1.417847000 | -0.531228000 |
| C | -2.871043000 | -1.623974000 | 0.830233000 |
| C | -3.884188000 | -1.073193000 | 1.619894000 |
| C | -4.950540000 | -0.252596000 | 0.916432000 |
| C | -4.354334000 | 0.457950000 | -0.285292000 |
| C | -3.312576000 | -0.185350000 | -0.958075000 |
| C | -3.821827000 | -1.309843000 | 2.998243000 |
| C | -2.779542000 | -2.067259000 | 3.545241000 |
| C | -1.764554000 | -2.580099000 | 2.729484000 |
| C | -1.792455000 | -2.352131000 | 1.346040000 |
| C | -2.628518000 | 0.376878000 | -2.041416000 |
| C | -3.049996000 | 1.630525000 | -2.505164000 |
| C | -4.111009000 | 2.287211000 | -1.871474000 |
| C | -4.746911000 | 1.713763000 | -0.764369000 |
| P | -0.445372000 | -2.765767000 | 0.163397000 |
| Pd | 0.500158000 | -0.827590000 | -1.060502000 |
| O | 1.808980000 | -0.771534000 | 0.547264000 |
| P | -1.134800000 | -0.515492000 | -2.627223000 |
| C | 1.444146000 | 0.775305000 | -1.918838000 |
| C | 1.928398000 | 0.710741000 | -3.226438000 |
| C | 2.569485000 | 1.805359000 | -3.830718000 |
| C | 2.711513000 | 2.985153000 | -3.103508000 |
| C | 2.259476000 | 3.063153000 | -1.782837000 |
| C | 1.638217000 | 1.960912000 | -1.156026000 |
| N | 1.207708000 | 2.002348000 | 0.168010000 |
| C | 1.518349000 | 3.131471000 | 1.018181000 |
| C | 0.970751000 | 2.900517000 | 2.421768000 |
| C | 1.132965000 | 4.093233000 | 3.351501000 |
| C | 0.850487000 | 3.843710000 | 4.822865000 |
| O | 1.466536000 | 5.184809000 | 2.944669000 |
| H | -0.938169000 | -3.139630000 | 3.174185000 |
| H | -4.594814000 | -0.894500000 | 3.650756000 |
| H | -2.747689000 | -2.246335000 | 4.622327000 |
| H | -2.535497000 | 2.106994000 | -3.343001000 |
| H | -4.431155000 | 3.266869000 | -2.232887000 |
| H | -5.556106000 | 2.251611000 | -0.262736000 |
| H | -0.994381000 | -3.902491000 | -0.497254000 |
| H | 0.459671000 | -3.438777000 | 1.018547000 |

| | | | |
|---|---|---|---|
| H | -1.703204000 | -1.676666000 | -3.221072000 |
| H | -0.824500000 | 0.213420000 | -3.798363000 |
| H | 1.805093000 | -0.207547000 | -3.810028000 |
| H | 2.940255000 | 1.728141000 | -4.856035000 |
| H | 2.409345000 | 3.988766000 | -1.225144000 |
| H | 3.193718000 | 3.856584000 | -3.555433000 |
| H | 1.348588000 | 1.092784000 | 0.617238000 |
| H | 2.608552000 | 3.334196000 | 1.082484000 |
| H | 1.069567000 | 4.051993000 | 0.611041000 |
| H | -0.109432000 | 2.665467000 | 2.368245000 |
| H | 1.433612000 | 2.012099000 | 2.888887000 |
| H | -0.081431000 | 3.272305000 | 4.961863000 |
| H | 1.665873000 | 3.236765000 | 5.252862000 |
| H | 0.795551000 | 4.799873000 | 5.359900000 |
| H | -5.767643000 | -0.921220000 | 0.580877000 |
| H | -5.407675000 | 0.469838000 | 1.609441000 |
| C | 2.881285000 | -1.537080000 | 0.685050000 |
| C | 3.581938000 | -1.531854000 | 1.919093000 |
| C | 4.699919000 | -2.340704000 | 2.113904000 |
| C | 5.164904000 | -3.186449000 | 1.097942000 |
| C | 4.487398000 | -3.199523000 | -0.125131000 |
| C | 3.366883000 | -2.391861000 | -0.334307000 |
| H | 3.220179000 | -0.874361000 | 2.714006000 |
| H | 5.218676000 | -2.311101000 | 3.077172000 |
| H | 6.042709000 | -3.817388000 | 1.256162000 |
| H | 4.838841000 | -3.844141000 | -0.936661000 |
| H | 2.855935000 | -2.389184000 | -1.302272000 |

**24:** E= -1905.238946

| | | | |
|---|---|---|---|
| 6 | 1.772250000 | -0.571403000 | 1.421370000 |
| 6 | 3.137703000 | -0.817785000 | 1.101556000 |
| 6 | 4.071151000 | -0.660651000 | 2.152658000 |
| 6 | 3.667443000 | -0.250460000 | 3.422876000 |
| 6 | 2.326718000 | 0.033165000 | 3.704205000 |
| 6 | 1.382726000 | -0.099347000 | 2.680180000 |
| 46 | 0.312826000 | -1.197136000 | 0.205968000 |
| 7 | 3.497337000 | -1.245906000 | -0.162248000 |
| 6 | 4.830119000 | -1.123110000 | -0.721568000 |
| 6 | 5.243907000 | 0.303666000 | -1.126704000 |
| 6 | 4.346860000 | 0.958243000 | -2.169729000 |
| 8 | 3.172685000 | 0.647905000 | -2.292284000 |
| 1 | 2.018499000 | 0.361964000 | 4.698543000 |
| 6 | 4.974107000 | 2.024276000 | -3.034532000 |
| 1 | 5.127385000 | -0.865856000 | 1.970846000 |
| 1 | 4.421598000 | -0.137935000 | 4.205819000 |
| 1 | 0.334678000 | 0.145845000 | 2.878035000 |
| 1 | 2.776276000 | -1.101290000 | -0.861543000 |
| 1 | 5.570349000 | -1.528684000 | -0.016251000 |
| 1 | 4.872855000 | -1.776346000 | -1.607531000 |
| 1 | 5.231146000 | 0.969325000 | -0.242092000 |
| 1 | 6.288245000 | 0.308904000 | -1.480845000 |
| 1 | 5.677719000 | 1.547805000 | -3.739392000 |
| 1 | 4.203197000 | 2.558930000 | -3.604349000 |
| 1 | 5.565974000 | 2.729493000 | -2.428875000 |
| 6 | -3.436406000 | -0.366755000 | -0.656554000 |
| 6 | -2.213550000 | 1.604274000 | -0.311790000 |
| 6 | -3.234758000 | -1.751462000 | -0.708731000 |
| 6 | -4.638392000 | 0.221303000 | -0.254786000 |
| 6 | -3.336118000 | 2.313657000 | 0.122859000 |
| 6 | -0.899848000 | 2.024436000 | -0.062910000 |
| 6 | -4.316501000 | -2.587334000 | -0.393749000 |

| | | | |
|---|---|---|---|
| 6 | -5.695055000 | -0.639019000 | 0.067496000 |
| 6 | -3.108766000 | 3.507965000 | 0.818377000 |
| 6 | -0.702107000 | 3.230157000 | 0.628524000 |
| 6 | -5.540633000 | -2.027506000 | -0.014694000 |
| 1 | -4.202621000 | -3.673379000 | -0.427483000 |
| 1 | -6.652043000 | -0.217494000 | 0.386106000 |
| 6 | -1.808301000 | 3.967550000 | 1.059670000 |
| 1 | -3.962530000 | 4.089047000 | 1.176925000 |
| 1 | 0.308484000 | 3.587587000 | 0.839865000 |
| 1 | -6.379261000 | -2.681695000 | 0.232221000 |
| 1 | -1.655584000 | 4.905149000 | 1.597815000 |
| 15 | -1.526439000 | -2.326528000 | -1.045174000 |
| 1 | -1.685713000 | -3.728395000 | -0.903836000 |
| 1 | -1.425980000 | -2.276711000 | -2.461442000 |
| 15 | 0.453464000 | 0.927557000 | -0.589309000 |
| 1 | 0.433520000 | 0.926495000 | -2.003013000 |
| 1 | 1.596982000 | 1.705033000 | -0.331586000 |
| 8 | -2.355810000 | 0.421316000 | -0.991745000 |
| 6 | -4.702679000 | 1.736002000 | -0.192811000 |
| 1 | -5.443298000 | 2.062490000 | 0.552529000 |
| 1 | -5.050821000 | 2.130967000 | -1.167063000 |

**TS-xant:** E= -1905.232499

| | | | |
|---|---|---|---|
| C | 1.691780000 | 1.002528000 | 0.992479000 |
| C | 2.987701000 | 0.472310000 | 1.222840000 |
| C | 3.825889000 | 1.186348000 | 2.098538000 |
| C | 3.403651000 | 2.394364000 | 2.666300000 |
| C | 2.143113000 | 2.922408000 | 2.387867000 |
| C | 1.279574000 | 2.215860000 | 1.535160000 |
| Pd | 0.486865000 | -0.445438000 | 0.321981000 |
| N | 3.303481000 | -0.763728000 | 0.641848000 |
| C | 4.623925000 | -1.371163000 | 0.748528000 |
| C | 5.671627000 | -0.786133000 | -0.212539000 |
| C | 5.292712000 | -0.903011000 | -1.685746000 |
| O | 4.141795000 | -1.104499000 | -2.032521000 |
| H | 1.824964000 | 3.870893000 | 2.825572000 |
| C | 6.406840000 | -0.748024000 | -2.692495000 |
| H | 4.814993000 | 0.797930000 | 2.347414000 |
| H | 4.082379000 | 2.931116000 | 3.333554000 |
| H | 0.282170000 | 2.615074000 | 1.328677000 |
| H | 2.986456000 | -0.840888000 | -0.325073000 |
| H | 4.980536000 | -1.302368000 | 1.786630000 |
| H | 4.509160000 | -2.446089000 | 0.536034000 |
| H | 5.836456000 | 0.289155000 | -0.011264000 |
| H | 6.651973000 | -1.265890000 | -0.049278000 |
| H | 7.054701000 | -1.641106000 | -2.656888000 |
| H | 5.993071000 | -0.646187000 | -3.704004000 |
| H | 7.045290000 | 0.116321000 | -2.449038000 |
| C | -3.364594000 | -1.135630000 | -0.235045000 |
| C | -2.815813000 | 1.019381000 | -0.979723000 |
| C | -2.740259000 | -2.279194000 | 0.277655000 |
| C | -4.680424000 | -0.775196000 | 0.064963000 |
| C | -4.094043000 | 1.518786000 | -0.720701000 |
| C | -1.693491000 | 1.840537000 | -1.153606000 |
| C | -3.498038000 | -3.133547000 | 1.092363000 |
| C | -5.406231000 | -1.640173000 | 0.893163000 |
| C | -4.236268000 | 2.911482000 | -0.666626000 |
| C | -1.866920000 | 3.232876000 | -1.107044000 |
| C | -4.826431000 | -2.813083000 | 1.389867000 |
| H | -3.051038000 | -4.039643000 | 1.508026000 |

| | | | |
|---|---|---|---|
| H | -6.439370000 | -1.393984000 | 1.152102000 |
| C | -3.140419000 | 3.759043000 | -0.870334000 |
| H | -5.220859000 | 3.341163000 | -0.464059000 |
| H | -1.015477000 | 3.903511000 | -1.245016000 |
| H | -5.411941000 | -3.479225000 | 2.026787000 |
| H | -3.278405000 | 4.841461000 | -0.834022000 |
| P | -0.946903000 | -2.462556000 | -0.058163000 |
| H | -0.655618000 | -3.637364000 | 0.680240000 |
| H | -0.903166000 | -3.026430000 | -1.361454000 |
| P | -0.082908000 | 1.009803000 | -1.320861000 |
| H | -0.125990000 | 0.346858000 | -2.572134000 |
| H | 0.787772000 | 2.081806000 | -1.608736000 |
| O | -2.592500000 | -0.331880000 | -1.047323000 |
| C | -5.216495000 | 0.518060000 | -0.521200000 |
| H | -6.001500000 | 0.939693000 | 0.124287000 |
| H | -5.698225000 | 0.309780000 | -1.496293000 |

**25:** E= -1905.247612

| | | | |
|---|---|---|---|
| C | 2.260560000 | 3.020911000 | -0.937128000 |
| C | 1.976192000 | 1.668280000 | -1.176051000 |
| C | 2.797841000 | 0.709852000 | -0.574749000 |
| C | 3.836782000 | 1.015879000 | 0.305964000 |
| C | 4.084602000 | 2.374235000 | 0.541697000 |
| C | 3.317741000 | 3.363865000 | -0.086330000 |
| C | 3.689917000 | -1.353080000 | 1.077097000 |
| C | 2.664719000 | -1.512001000 | 0.143269000 |
| C | 1.731252000 | -2.552683000 | 0.185068000 |
| C | 1.862349000 | -3.522382000 | 1.189753000 |
| C | 2.897328000 | -3.407295000 | 2.123882000 |
| C | 3.789924000 | -2.328909000 | 2.077319000 |
| H | 1.659449000 | 3.805371000 | -1.403473000 |
| H | 4.889540000 | 2.663865000 | 1.222211000 |
| H | 3.540522000 | 4.416751000 | 0.098633000 |
| H | 1.157648000 | -4.354593000 | 1.255869000 |
| H | 3.000767000 | -4.160701000 | 2.907338000 |
| H | 4.576714000 | -2.246210000 | 2.831739000 |
| P | 0.525973000 | 0.997025000 | -2.075459000 |
| H | 1.086465000 | 0.504807000 | -3.284182000 |
| H | -0.048684000 | 2.187150000 | -2.589818000 |
| P | 0.356016000 | -2.447975000 | -1.013276000 |
| H | 0.965269000 | -2.675088000 | -2.273562000 |
| H | -0.293248000 | -3.688357000 | -0.826734000 |
| Pd | -0.991416000 | -0.587456000 | -0.898746000 |
| C | -2.504435000 | -1.617632000 | -0.056859000 |
| C | -2.908357000 | -2.900190000 | 0.313392000 |
| C | -3.389096000 | -0.551408000 | 0.078460000 |
| C | -4.208919000 | -3.070926000 | 0.814189000 |
| H | -2.256597000 | -3.772631000 | 0.223319000 |
| C | -4.685818000 | -0.697901000 | 0.564417000 |
| C | -5.088415000 | -1.988044000 | 0.934554000 |
| H | -4.542269000 | -4.069195000 | 1.109078000 |
| H | -5.369682000 | 0.149771000 | 0.656007000 |
| H | -6.097604000 | -2.149875000 | 1.319682000 |
| N | -2.731890000 | 0.691363000 | -0.353650000 |
| H | -3.211468000 | 1.082118000 | -1.168613000 |
| C | -2.637616000 | 1.725042000 | 0.708390000 |
| H | -3.647039000 | 1.957174000 | 1.087432000 |
| H | -2.084840000 | 1.296551000 | 1.555107000 |
| C | -1.969042000 | 3.007928000 | 0.237328000 |
| H | -0.935475000 | 2.815580000 | -0.101853000 |
| H | -2.495982000 | 3.450875000 | -0.627862000 |

| | | | |
|---|---|---|---|
| C | -1.894032000 | 4.050013000 | 1.359457000 |
| O | -2.201578000 | 3.756031000 | 2.491363000 |
| C | -1.426972000 | 5.435814000 | 0.972893000 |
| H | -0.517265000 | 5.395113000 | 0.352396000 |
| H | -2.206672000 | 5.933003000 | 0.370446000 |
| H | -1.242143000 | 6.031095000 | 1.876291000 |
| C | 4.594322000 | -0.141108000 | 0.933956000 |
| H | 5.460795000 | -0.402798000 | 0.296114000 |
| H | 5.009291000 | 0.151027000 | 1.910184000 |
| O | 2.496087000 | -0.598864000 | -0.869697000 |

**14-xant-B:** E= -1905.247155

| | | | |
|---|---|---|---|
| C | -3.226790000 | -1.743494000 | -1.092015000 |
| C | -2.379882000 | -0.952049000 | -0.305922000 |
| C | -2.535031000 | -0.936849000 | 1.089639000 |
| C | -3.517718000 | -1.739362000 | 1.690531000 |
| C | -4.355220000 | -2.536165000 | 0.904379000 |
| C | -4.221229000 | -2.524035000 | -0.487203000 |
| Pd | -0.911688000 | 0.298262000 | -0.946429000 |
| O | -2.001126000 | 2.127392000 | -0.391596000 |
| C | -2.733823000 | 2.632976000 | 0.457527000 |
| C | -3.061329000 | 4.097329000 | 0.361595000 |
| N | -1.708729000 | -0.018222000 | 1.834522000 |
| C | -2.426866000 | 1.058580000 | 2.513196000 |
| C | -3.366116000 | 1.853811000 | 1.586001000 |
| P | 0.108090000 | -1.603387000 | -1.660690000 |
| C | 1.371617000 | -2.317937000 | -0.550747000 |
| C | 2.463830000 | -1.494211000 | -0.258373000 |
| C | 3.442803000 | -1.813279000 | 0.684372000 |
| C | 3.323973000 | -3.053909000 | 1.324372000 |
| C | 2.266733000 | -3.921915000 | 1.022357000 |
| C | 1.282808000 | -3.559068000 | 0.095746000 |
| O | 2.509344000 | -0.298543000 | -0.932220000 |
| C | 2.987469000 | 0.784000000 | -0.228818000 |
| C | 4.002820000 | 0.616605000 | 0.714888000 |
| C | 4.535267000 | -0.788796000 | 0.936532000 |
| C | 4.437053000 | 1.766219000 | 1.386799000 |
| C | 3.866515000 | 3.015427000 | 1.112353000 |
| C | 2.827231000 | 3.141464000 | 0.183405000 |
| C | 2.360933000 | 2.005865000 | -0.494687000 |
| P | 0.890258000 | 1.918374000 | -1.589321000 |
| H | -4.081751000 | 1.154714000 | 1.117000000 |
| H | -3.127209000 | -1.759285000 | -2.181116000 |
| H | -1.105822000 | -0.504804000 | 2.496586000 |
| H | 0.785524000 | -1.463497000 | -2.898589000 |
| H | -0.716030000 | -2.715384000 | -1.939785000 |
| H | -4.885330000 | -3.131266000 | -1.107696000 |
| H | -5.116381000 | -3.161195000 | 1.377243000 |
| H | -3.630849000 | -1.733417000 | 2.778854000 |
| H | -3.064686000 | 0.697593000 | 3.346003000 |
| H | -1.681392000 | 1.735985000 | 2.962958000 |
| H | 0.507830000 | 3.281568000 | -1.643612000 |
| H | 1.461687000 | 1.804637000 | -2.885529000 |
| H | -2.589956000 | 4.551678000 | -0.518686000 |
| H | -4.155428000 | 4.230549000 | 0.312010000 |
| H | -2.728640000 | 4.612321000 | 1.279247000 |
| H | 0.448132000 | -4.233870000 | -0.108352000 |
| H | 2.201170000 | -4.888667000 | 1.525783000 |
| H | 4.068672000 | -3.347465000 | 2.068965000 |
| H | 2.375975000 | 4.119513000 | 0.000039000 |

| | | | |
|---|---|---|---|
| H | 4.228606000 | 3.901239000 | 1.638438000 |
| H | 5.232151000 | 1.685552000 | 2.132761000 |
| H | 5.380098000 | -0.975533000 | 0.245535000 |
| H | 4.941366000 | -0.895317000 | 1.953603000 |
| H | -3.960257000 | 2.539012000 | 2.207548000 |

**TS1-xant-B:** E= -1905.178227

| | | | |
|---|---|---|---|
| C | -4.657024000 | 1.232305000 | 0.568471000 |
| C | -3.416900000 | 2.103856000 | 0.470358000 |
| C | -2.373329000 | 1.648312000 | -0.337121000 |
| O | -2.495098000 | 0.462346000 | -1.023427000 |
| C | -3.179422000 | -0.539599000 | -0.373134000 |
| C | -4.276957000 | -0.232184000 | 0.432631000 |
| C | -3.217966000 | 3.320714000 | 1.135061000 |
| C | -2.020398000 | 4.032629000 | 0.988779000 |
| C | -0.978387000 | 3.529723000 | 0.202329000 |
| C | -1.146481000 | 2.307316000 | -0.465592000 |
| C | -4.920346000 | -1.305689000 | 1.061763000 |
| C | -4.468041000 | -2.619420000 | 0.883594000 |
| C | -3.341486000 | -2.890642000 | 0.099531000 |
| C | -2.671667000 | -1.832939000 | -0.533560000 |
| P | 0.155762000 | 1.408606000 | -1.378398000 |
| Pd | 0.761225000 | -0.730520000 | -0.645077000 |
| P | -1.092066000 | -1.963655000 | -1.441807000 |
| C | 2.795106000 | -0.086321000 | -0.073078000 |
| C | 3.508996000 | 0.854807000 | 0.710507000 |
| C | 4.403229000 | 1.737556000 | 0.071369000 |
| C | 4.687417000 | 1.602726000 | -1.287486000 |
| C | 4.156242000 | 0.527341000 | -2.011702000 |
| C | 3.244034000 | -0.331414000 | -1.389787000 |
| N | 3.422043000 | 0.771234000 | 2.098965000 |
| C | 3.802880000 | -0.524225000 | 2.715072000 |
| C | 3.419070000 | -1.749693000 | 1.866593000 |
| C | 2.043313000 | -1.562123000 | 1.229435000 |
| C | 1.004106000 | -1.040859000 | 2.237052000 |
| O | 1.590891000 | -2.384689000 | 0.328731000 |
| H | 4.163056000 | -1.986999000 | 1.096774000 |
| H | 2.864372000 | -1.188626000 | -1.958346000 |
| H | 3.883105000 | 1.544797000 | 2.570607000 |
| H | -0.243024000 | 1.488177000 | -2.737419000 |
| H | 1.224700000 | 2.334294000 | -1.374634000 |
| H | 4.458125000 | 0.349700000 | -3.046170000 |
| H | 5.390971000 | 2.290455000 | -1.763209000 |
| H | 4.934541000 | 2.483077000 | 0.671089000 |
| H | 4.892739000 | -0.559284000 | 2.896586000 |
| H | 3.313873000 | -0.581587000 | 3.699209000 |
| H | -0.842813000 | -3.355667000 | -1.425188000 |
| H | -1.448357000 | -1.780777000 | -2.802865000 |
| H | -0.010722000 | -1.084047000 | 1.819042000 |
| H | 1.028366000 | -1.715663000 | 3.111464000 |
| H | 1.216340000 | -0.022036000 | 2.580080000 |
| H | -0.038229000 | 4.080783000 | 0.123935000 |
| H | -1.891360000 | 4.984311000 | 1.508322000 |
| H | -4.008515000 | 3.718077000 | 1.777033000 |
| H | -2.981126000 | -3.916903000 | -0.002572000 |
| H | -4.990620000 | -3.441890000 | 1.376244000 |
| H | -5.785983000 | -1.113780000 | 1.701189000 |
| H | -5.364123000 | 1.506017000 | -0.238362000 |
| H | -5.185949000 | 1.411582000 | 1.516223000 |
| H | 3.352243000 | -2.627290000 | 2.535900000 |

**15-xant-B:** E= -1905.226754

| | | | |
|---|---|---|---|
| C | -4.601544000 | -0.081868000 | 1.426947000 |
| C | -3.818804000 | 1.190543000 | 1.148416000 |
| C | -2.945488000 | 1.182815000 | 0.059796000 |
| O | -2.836476000 | 0.060044000 | -0.730380000 |
| C | -2.918030000 | -1.143292000 | -0.068907000 |
| C | -3.786397000 | -1.294912000 | 1.012274000 |
| C | -3.878372000 | 2.369809000 | 1.901873000 |
| C | -3.087940000 | 3.477086000 | 1.567738000 |
| C | -2.191721000 | 3.422410000 | 0.494845000 |
| C | -2.103744000 | 2.249683000 | -0.270059000 |
| C | -3.808386000 | -2.551593000 | 1.631593000 |
| C | -2.986741000 | -3.592794000 | 1.179162000 |
| C | -2.094696000 | -3.396241000 | 0.119612000 |
| C | -2.047904000 | -2.144456000 | -0.512458000 |
| P | -0.870284000 | 1.918506000 | -1.578015000 |
| Pd | 0.587869000 | 0.079768000 | -1.262346000 |
| P | -0.849538000 | -1.636422000 | -1.783189000 |
| C | 3.135186000 | 0.196589000 | 0.276032000 |
| C | 4.141803000 | 0.463999000 | 1.234473000 |
| C | 4.487791000 | 1.811528000 | 1.487204000 |
| C | 3.900375000 | 2.855355000 | 0.770166000 |
| C | 2.991090000 | 2.592256000 | -0.257596000 |
| C | 2.642491000 | 1.253418000 | -0.503605000 |
| N | 4.745279000 | -0.583499000 | 1.883077000 |
| C | 4.666093000 | -1.979318000 | 1.451669000 |
| C | 3.854208000 | -2.150789000 | 0.158650000 |
| C | 2.615602000 | -1.229749000 | 0.164009000 |
| C | 1.710482000 | -1.543786000 | 1.381751000 |
| O | 1.887776000 | -1.418603000 | -1.030299000 |
| H | 4.459643000 | -1.895749000 | -0.724440000 |
| H | 2.240065000 | 1.037100000 | -1.526956000 |
| H | 5.473712000 | -0.354454000 | 2.547970000 |
| H | -1.615769000 | 1.915399000 | -2.784865000 |
| H | -0.224584000 | 3.172455000 | -1.697936000 |
| H | 2.612132000 | 3.397485000 | -0.889790000 |
| H | 4.196226000 | 3.884295000 | 0.987848000 |
| H | 5.239933000 | 2.035718000 | 2.248793000 |
| H | 5.684871000 | -2.372963000 | 1.292594000 |
| H | 4.219326000 | -2.589401000 | 2.256883000 |
| H | -0.123203000 | -2.807192000 | -2.081427000 |
| H | -1.617611000 | -1.435966000 | -2.957462000 |
| H | 0.816138000 | -0.899999000 | 1.364504000 |
| H | 1.384358000 | -2.595121000 | 1.335216000 |
| H | 2.214835000 | -1.373930000 | 2.343751000 |
| H | -1.556822000 | 4.282499000 | 0.269732000 |
| H | -3.158015000 | 4.389473000 | 2.163392000 |
| H | -4.549461000 | 2.424797000 | 2.763023000 |
| H | -1.434093000 | -4.205988000 | -0.198552000 |
| H | -3.029004000 | -4.566086000 | 1.672172000 |
| H | -4.474391000 | -2.720184000 | 2.481874000 |
| H | -5.550453000 | -0.063487000 | 0.856917000 |
| H | -4.879984000 | -0.143578000 | 2.489275000 |
| H | 3.548042000 | -3.202868000 | 0.055876000 |